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Ultra-fast laser pulses provide an ion source for highly selective mass spectroscopy

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ABSTRACT The mass spectra of two isomers of butane, 1-butene and cis-2-butene, interacting with linearly polarized Ti:sapphire laser pulses, were compared. It was demonstrated that the difference between the two spectra are much more pronounced than the corresponding spectra prepared by 100 eV electron ionization ion source. In addition, the difference could be varied by changing the peak laser intensity. The observation suggests potential application of dissociative multiphoton ionization by ultrafast laser pulses as a source for high performance mass spectroscopy.

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1 Introduction

Electron ionization is widely used as a low cost and practical ion source for mass spectroscopy. However, this source may not provide the optimum performance when the simultaneous analysis of mixtures containing multiple isomers is required. Let us take, as an example, the mass spectra of butane isomers studied by Bennett and Cook [1]. Visual inspection of the reported results indicates that the differences between the mass spectra of different isomers are not sufficient for accurately quantifying the partial concentrations of the isomers in a mixture. Any source capable of increasing the difference would improve the accuracy by which the concentration of each isomer is determined. A potential candidate for an appropriate source is offered by the dissociative multiphoton/tunnel ionization of molecules in strong laser field, which is induced by the ionization of inner valence electrons [2, 3]. According to the model presented in these references, the fragmentation pattern of polyatomic molecules interacting with ultrafast laser pulses are mainly determined by the electronic configuration of the first few higher energy orbitals of the molecule and the wavelength and the peak intensity of the laser field. Therefore, it is expected that the resulting mass spectra of two isomers will have appreciable differences due to the fact that the electronic structure of the high lying orbitals are sensitive to the geometry of

the molecule. In order to verify this statement, we studied the fragmentation of 1-butene and cis-2-butene interacting with femtosecond Ti:sapphire laser pulses. The resulting fragmentation patterns were compared for the two isomers and it was shown that their difference, as quantified by the spectral similarity index (SI) [1] or the match factor [4], was more pronounced than the case of using 100 eV electrons as an ionization/dissociation source [1]. This suggests the suitability of strong laser pulse induced dissociative ionization of polyatomic molecules for providing an highly selective ion source for mass spectroscopy. In addition, by demonstrating the dependence of SI on the peak laser intensity, a practical means for optimizing the ion source in terms of sensitivity and selectivity is presented.

2 Experimental setup

The experimental set-up has already been described in [5]. Briefly, a Ti:sapphire laser system provides a train of 800 nm transform limited pulses having a full-width-at-half-maximum time duration of 175 fs. The linearly polarized pulses were focused using a lens with a focal length of 100 cm into a high vacuum chamber having a background pressure of 4×10^{-9} Torr. The pressure of the gas, either 1-butene or cis-2-butene, in the chamber was set at 10^{-7} Torr. Ion species were separated with a time-of-flight mass spectrometer and the ion signals were measured by an oscilloscope.

As it will be seen in Sect. 3, the peak laser intensity is the main parameter determining the difference in the mass spectra of isomers. Therefore, we offer a practical intensity calibration method to enable using this quantity, alongside laser wavelength, to label the mass spectra of different molecules. This is analogous to the common practice of using electron energy for specifying and tabulating the mass spectra of molecules using an electron ionization source. In order to establish the intensity calibration procedure, through direct measurement, it was found that the fluctuation of the pulse width had a CV (coefficient of variation; standard deviation divided by the average value) of less than $\pm 1.5\%$ and were not correlated to the fluctuation of the pulse energy. In addition, as a result of stable beam shape, the focal spot size did not have noticeable fluctuation and had a CV around 2%. Therefore, measuring the pulse energy would suffice for measuring

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or monitoring the peak intensity. For this purpose, a part of the pulse was taken off from a reflection of a wedged beam splitter situated after the interaction region and was detected with a pyroelectric energy-meter.

After recording the spectra of Butane along with the shot to shot energy-meter reading, the peak intensity was calculated by multiplying the energy-meter reading with a conversion factor. The conversion factor was determined in the following manner. Without changing the experimental setup, the vacuum chamber was filled with Xe at a pressure of 5×10^{-8} Torr. Then the ion signal of Xe^+ was recorded at different pulse energies and the ion signal versus energy-meter reading was plotted in a log–log graph. The resulting plot, presented in Fig. 1, represents the intensity dependence of multiphoton/tunnel ionization of Xe around the saturation region, where the plot asymptotically approaches a $I_0^{3/2}$ dependence (I_0 being the peak intensity). This behavior is known as the saturation of ion curve [6] and can be used to determine the saturation intensity by locating the saturation point. Note that in practice, depending on the experimental setup, the exponent might be less than 3/2. Regardless of the exact value of the exponent, the saturation point is determined by drawing two lines tangent to the ion versus intensity (energy-meter signal) in a log–log plot and defining the intersection of the two lines as the saturation point. This point provides a fixed point for calculating the conversion factor between the energy-meter reading on one experiment to the established peak intensity of another test performed using lasers with the same wavelength and pulse duration. For the present results we compared the saturation point of Fig. 1 with the saturation point of the Xe^+ vs. “peak intensity” plot of [7] that had been prepared under similar experimental conditions. This provided a conversion factor of 3.95×10^{16} between the energy-meter reading to peak laser intensity. We should mention that [7] has established the absolute intensity calibration based on comparison of the saturation intensity of Xe^+ with

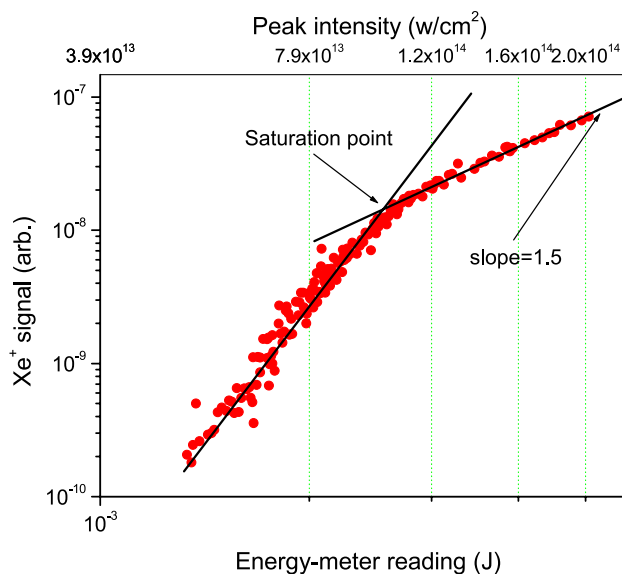


FIGURE 1 Xe^+ signal vs. the reading of the energy-meter for intensity calibration. As was explained in the text, the peak intensity at the upper part of graph is given by multiplying the energy-meter reading by a factor of 3.95×10^{16}

the saturation intensity of He^+ . The saturation intensity of He^+ had been determined by comparing the measured data with the predictions of the ADK model [8]. It should be mentioned that we could have used He, instead of Xe, for peak intensity calibration. However, reaching to the saturation point of He requires very high laser power.

3 Experimental results

The mass spectra of 1-butene and cis-2-butene were recorded at two different peak laser intensities and presented in Figs. 2 and 3. In both figures the signal corresponding to singly charged ion of cis-2-butene, at the mass to charge ratio of $m/q = 56$, has been scaled to an arbitrary value of 100 and the peaks corresponding to other ions have been accordingly scaled. As it is observed at both peak intensities the difference in the spectra of the isomers are more pronounced than the cases of using electron impact ionization of [1].

In order to quantify the performance of the new ion source in terms of determining the composition of a gas containing the two isomers, we calculate the similarity index (SI), which is defined as [4],

$$\text{SI} \equiv \left(\sum_{m/q} \sqrt{I_x I_y} \right)^2 / \left(\sum_{m/q} I_x \sum_{m/q} I_y \right), \quad (1)$$

where x and y denote the two isomers, m and q are the mass and charges of a given ion, and I_x and I_y are the relative abundances of peaks for equal value of m/q on 1-butene or cis-2-butene mass spectra. The SI values were calculated to be $\text{SI} = 0.793$ and $\text{SI} = 0.918$ for the spectra presented in Figs. 2 and 3, respectively. The corresponding value reported in [1], in the case of using electron source for ionization, is $\text{SI} = 0.9957$. This observation readily indicates that the dissociative ionization by ultra-fast laser pulses can potentially provide a high performance ion source for applications in mass spectroscopy. In addition, the dependence of the SI on the laser peak intensity could provide a practical optimiza-

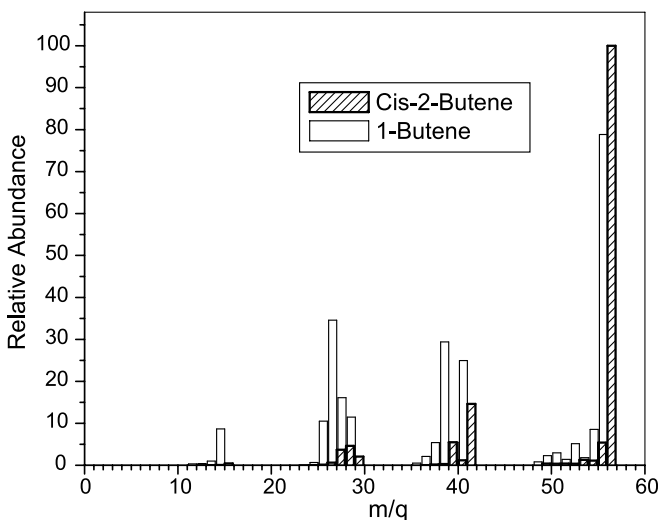


FIGURE 2 Comparison of mass spectra for cis-2-Butene and 1-Butene prepared by exposing pure gases to linearly polarized short laser pulses focused to a peak intensity of 2×10^{13} W/cm² ($\text{SI} = 0.793$)

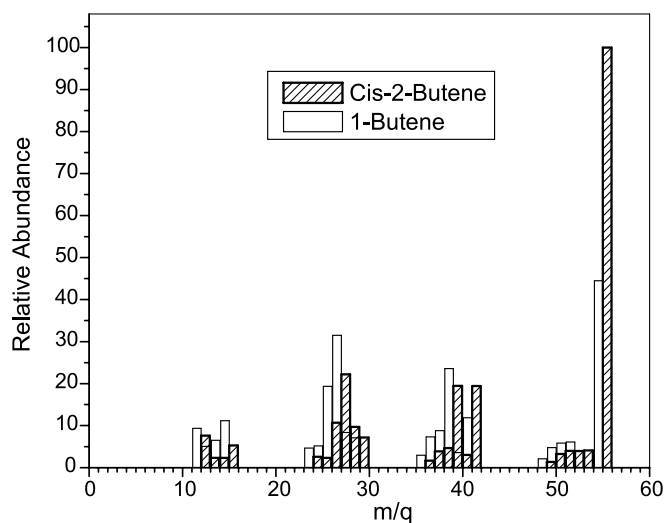


FIGURE 3 Comparison of mass spectra for cis-2-Butene and 1-Butene prepared by exposing pure gases to linearly polarized short laser pulses focused to a peak intensity of 6.5×10^{13} W/cm² (SI = 0.918)

tion tool. We elaborate on these observations in the following section.

4 Discussion

As mentioned in the introduction, the dissociative ionization of polyatomic molecules interacting with strong ultra-fast laser pulses occurs via the following process [2, 3]. First, multiphoton/tunnel ionization of electrons from the inner valence orbitals results in the excitation of molecular ions into some ro-vibrational levels of an excited electronic state. The ions could undergo rapid radiationless transition to some high-lying ro-vibrational level belonging to a lower electronic state and the excited ions could dissociate via various fragmentation channels, or they could dissociate directly in to fragments.

The peak laser intensity is the main parameter that can be used to optimize the dissociative multiphoton ionization as a source for high performance mass spectroscopy. This is due to the action of two well established phenomena; an increase in the ionization potential resulting from ac Stark shift and the field induced barrier suppression. Let us denote the appearance potential of a particular fragment by AP, which is defined as the minimum energy needed to form the fragment from a neutral molecule in the ground state. AP can be expressed as $AP = E_i + \Delta E$, where E_i is one of the ionization potentials (from the inner valence orbital) and ΔE is the minimum energy above that ionization potential needed to form the ion. At the peak laser intensity, I_0 , E_i increases by the so-called ponderomotive potential $Up_{(ev)} = 9.33 \times 10^{-14} I_0(\text{W/cm}^2) \lambda^2(\mu\text{m})^2$, where λ is the wavelength of laser. The ponderomotive potential is the average energy of the oscillatory motion of a free electron in an electromagnetic field and explicitly appears in analytical formula for the multiphoton ionization of atoms on applying the strong field approximation [9, 10]. In contrast to the ionization potential, ΔE decreases by an amount δE due to field induced barrier suppression [2, 11, 12]. The magnitude of δE is esti-

mated to be given by $\delta E \approx 0.5FR$, where F is the strength of the laser field and R is the size of the parent ion [13]. For example at a peak intensity of 2×10^{13} W/cm² and for an ion with $R = 2$ atomic unit, δE is calculated to be 0.62 eV.

The aforementioned arguments can be applied to qualitatively explain the dependence of SI on the peak laser intensity. For this purpose we define partial SI by excluding the signal of the parent ion from the summations in (1). This quantity is calculated to be SI = 0.868 and SI = 0.967 at low and high intensities, respectively. The relatively elevated value of the partial SI indicates that at higher intensities the fragmentation patterns of the two isomers are more similar. This can be explained by noting that the quantity δE at higher intensity (6.5×10^{13} W/cm²) is higher than its value at the low intensity (2×10^{13} W/cm²) by a factor of 1.8. Consequently, most of the parent ions resulting from the multiphoton/tunnel ionization of inner valence electrons will indiscriminately dissociate at higher intensities resulting in a mass spectrum that is independent of the differences in the geometries of the isomers. One might conclude that lower intensities are preferable for giving rise to smaller partial SI. However, we should remember that the ion signal decreases rapidly with lowering of the intensity, and the potential gain due to reduced SI might be compromised by the detection limit of the mass spectrometer. Therefore, a balance between (partial) SI and the magnitude of the ion signal would lead to an optimum ion source.

5 Conclusion

The dissociative multiphoton/tunnel ionization of polyatomic molecules interacting with strong ultra-fast laser pulses was suggested as an appropriate source for the mass spectroscopy of isomers. The suggestion was tested in the case of 1-butene and cis-2-butene. The results were qualitatively explained and it was shown that the laser intensity can be used to optimize the ion source.

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REFERENCES

- 1 K.H. Bennett, K.D. Cook, *J. Am. Soc. Mass Spectrum* **11**, 1079 (2000)
- 2 A. Talebpour, A.D. Bandrauk, J. Yang, S.L. Chin, *Chem. Phys. Lett.* **313**, 789 (1999)
- 3 A. Talebpour, A.D. Bandrauk, K. Vijayalakshmi, S.L. Chin, *J. Phys. B* **33**, 4615 (2000)
- 4 S.E. Stein, *J. Am. Soc. Mass Spectrum* **6**, 644 (1995)
- 5 S. Larochelle, A. Talebpour, S.L. Chin, *J. Phys. B* **31**, 1201 (1998)
- 6 M.R. Cervenak, N.R. Isenor, *Opt. Commun.* **13**, 175 (1975)
- 7 S. Larochelle, A. Talebpour, S.L. Chin, *J. Phys. B* **31**, 1215 (1998)
- 8 M.V. Ammosov, N.B. Delone, V.P. Krainov, *Sov. Phys. JETP* **64**, 1191 (1986)
- 9 F.H.M. Faisal, *J. Phys. B* **6**, L89 (1973)
- 10 H.R. Reiss, *Phys. Rev. A* **22**, 1786 (1980)
- 11 P. Dietrich, P.B. Corkum, *J. Chem. Phys.* **97**, 3187 (1992)
- 12 A. Conjusteau, A.D. Bandrauk, P.B. Corkum, *J. Chem. Phys.* **106**, 9095 (1992)
- 13 A.D. Bandrauk, *Molecules in Laser Fields* (Marcel Dekker, New York, 1994), Chapt. 3