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Gas phase studies on terpenes by ion mobility spectrometry using different atmospheric pressure chemical ionization techniques

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Abstract

The ionization pathways and drift behavior were determined for sets of constitutional isomeric and stereoisomeric non-polar hydrocarbons (unsaturated monocyclic terpenes, unsaturated and saturated bicyclic terpenes) using ion mobility spectrometry (IMS) with different techniques of atmospheric pressure chemical ionization (APCI) to assess how structural and stereochemical differences influence ion formation. Depending on the structural features, different ions were observed for constitutional isomers using ion mobility spectrometry with photoionization (PI) and corona discharge (CD) ionization. Photoionization provides ion mobility spectra containing one major peak for saturated compounds while at two peaks were observed for unsaturated compounds, which can be assigned to product ions related to monomer and dimer ions. However, differences in relative abundance of product ions were found depending on the position of the double bond. Although IMS using corona discharge ionization permits the most sensitive detection of non-polar hydrocarbons, the spectra are complex and differ from those obtained using photoionization. Additional cluster ions and fragment ions were detected. Only small differences in ion mobility spectra were observed for the diastereomers while the enantiomers provide identical spectra. The structure of the product ions formed was checked by investigations using the coupling of ion mobility spectrometry with mass spectrometry (IMS–MS).

Keywords: Ion mobility spectrometry; Mass spectrometry; Photoionization; Corona discharge ionization; Terpenes

1. Introduction

Ion mobility spectrometry (IMS) permits the rapid and simple on-site determination of gaseous compounds by fieldable and hand-held devices [1,2]. The principle of IMS is based on determining the drift velocities (v_d) attained by ionized sample molecules in the weak electric field of a drift tube at atmospheric pressure. Therefore, ions have to be formed from sample molecules to measure ion mobilities.

^{63}Ni ionization sources are commonly used in IMS for the ionization of neutral sample molecules [3,4]. ^{63}Ni emits beta particles (electrons). The emitted electrons collide with the molecules of the carrier- or drift gas. The most of spectrometers work with nitrogen or air as drift- and/or carrier gas. Using these gases, series of reactions are initiated by these collisions. Reactant ions with the structure $H^+(H_2O)_n$ are mainly formed as a result of these processes. Positive ions of substances investigated are formed mainly via proton-transfer reactions [5]. Photoionization (PI) and corona discharge (CD) ionization were developed as alternative non-radioactive ionization sources. IMS using PI enables compounds (M) to be determined whose ionization energies are below the energy (10–12 eV) emitted by the radiation source, the most probable ionization pathway producing M^+ ions [6]. Using CD ionization, positive ions may be formed via different processes due to the varying strength of the electric field around the corona needle. Electron impact, photoionization and proton-transfer reactions lead to the product ions of substances investigated

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[7]. For all the aforementioned techniques, many or all the different ions present in the mobility spectra may result from ion–molecule reactions subsequent to the initial ionization [8].

The ions are separated within the drift tube and the drift velocities are determined. The drift velocity (v_d) is proportional to the strength of the electric field (E) with the constant of proportionality being the mobility (K) of the ions. K is derived using Eq. (1).

$$K = \frac{v_d}{E} \tag{1}$$

Ion mobility is influenced by the operational parameters used (e.g., drift gas and temperature) as well as by the masses of the ions and their collisional cross-sections. The influence of these parameters on ion mobility can be expressed [9,10] as

$$K = \left(\frac{3q}{16N}\right) \times \left(\frac{2\pi}{\mu kT}\right)^{1/2} \times \left(\frac{1+\alpha}{\Omega_D}\right) \tag{2}$$

where q is the charge of the ion, N the density of drift gas molecules, $\mu = (m \times M)/(m + M)$ the reduced mass of the ion (m) and drift gas molecule (M), k the Boltzmann constant, T the temperature (K), α the correction factor ($\alpha < 0.02$ for $m > M$) and Ω_D is the average ionic collision cross-section. Ω_D includes structural parameters (physical size and shape) and the electronic factors describing the ion–neutral interaction forces [11,12].

The application of identical operational parameters (drift gas, gas flows and temperature) limits the number of variables influencing the ion mobilities of various compounds to ionic mass (m) and structure (Ω_D). The influence of ionic mass on ion mobility can be described by mass-to-mobility correlation lines, which are known for a large number of substances.

These mass-to-mobility correlation lines demonstrate to a sufficient approximation, that mass effects are the dominating parameters. Structural differences are of minor importance, but cannot be ruled out. As known from literature for ^{63}Ni ionization, structural differences can entail errors in the correlation between ionic mass and ion mobility of between 5% and 20% [13].

In former papers, we described the influence of structural features on ion mobility spectra [14–16]. For these studies, we investigated sets of isomeric hydrocarbons. Investigating isomers with identical molecular weights enables mass effects to be ruled out. Additionally, polar effects can be minimized by investigating hydrocarbons, rather than substances containing polar functional groups. Our recent studies of alkylated benzenes, cycloalkanes and cycloalkenes with different constitution (constitutional isomers) have revealed that different ionization techniques provide distinct differences, depending on structure, in the ion mobility spectra and in the observable concentration ranges of isomeric compounds.

In this paper, we have extended these studies by investigating stereoisomeric hydrocarbons using CD ionization and PI to assess the influence of molecular structure on the ion mobility and ionization pathways. For our purpose, we selected a set of monoterpenes, which included monocyclic (isomers of limonene and terpinene) as well as saturated (isomers of pinane) and unsaturated (isomers of pinene) bicyclic monoterpenes. These compounds, produced by trees and plants, are emitted into the atmosphere due their significant vapor pressure at room temperature [17]. Therefore, terpenes are important in atmospheric chemistry [18].

The isomeric terpenes investigated can be classified as constitutional (structural) isomers and stereoisomers.

Alpha- and gamma-terpinene as well as alpha- and beta-pinene are constitutional isomers due to their differences in the connectivity of atoms within the molecule. Furthermore, limonene and terpinene are hydrocarbons with different constitutions. Constitutional isomers vary in their physical and chemical properties and can be differentiated using spectroscopic methods.

Stereoisomers can be subdivided into enantiomers and diastereomers.

Stereoisomers are signified as enantiomers, if the isomers are superimposable on their mirror image. In most cases, the premise for the existence of enantiomers is the presence of one asymmetric carbon atom. Enantiomers normally exhibit the same chemical and physical properties and cannot be distinguished using spectroscopic methods. *R*(+)- and *S*(−)-limonene, (+)-alpha- and (−)-alpha-pinene, (+)-beta- and (−)-beta-pinene, (1*R*)-*cis*- and (1*S*)-*cis*-pinane, (1*R*)-*trans*- and (1*S*)-*trans*-pinane can be assigned as enantiomers.

Stereoisomers, which are not the mirror image of each other, are signified diastereomers. Compounds with two or more asymmetric carbon atoms belong to this group. Spectroscopic methods are normally able to differentiate between diastereomers due to their different chemical and physical properties. (1*R*)-*trans*- and (1*S*)-*cis*-pinane are diasteriomers as well as are (1*R*)-*cis*- and (1S)-*trans*-pinane.

2. Experimental

2.1. Ion mobility measurements

The substances used in this study (unsaturated monocyclic terpenes, unsaturated and saturated bicyclic terpenes) had a purity of about 99% and were obtained from Fluka. Their purity was verified by gas-chromatography. The details of the IMS sample introduction system and its operation have been described previously [19].

A series of measurements with increasing sample concentration were carried out for each compound in order to assess any correlation between ion mobility spectra and concentration. The measurements were started with the visual formation of product ions up to a decrease in reactant ion intensity of about 80% (CD ionization).

The measurements were performed with RAID 1 ion mobility spectrometers (BRUKER, Leipzig, Germany). With the exception of the method of ionization, identical operational parameters (gas flow, temperatures in ionization region and drift tube) were used for all the measurements. The PI source was equipped with a krypton lamp providing 10 eV and 10.6 eV photons. The basic features of the CD ionization source used in this study have been described in detail [7].

The spectrometers are equipped with a membrane inlet and operated with a bi-directional flow system [13]. The operational parameters used to obtain the spectra were: temperature of inlet system, 80 °C; carrier gas flow rate, 25 l/h; drift gas flow rate, 25 l/h; electric field, 245 V/cm; temperature of drift tube, 80 °C; pressure, atmospheric pressure. Air was used as the carrier gas and drift gas.

The reduced mobility values (K_0 values) were calculated according to the conventional equation [20]:

$$K_0 = \left(\frac{d}{t \times E}\right) \times \left(\frac{p}{760}\right) \times \left(\frac{273}{T}\right) \quad (\mathrm{cm^2/(V\,s)}) \qquad (3)$$

where d is the drift length (cm), t the drift time (s), E the field strength (V/cm), p the pressure (Torr) and T is the temperature (K).

A series of positive ion mobility spectra was obtained for each sample. After equilibrium, 30 spectra (16 accumulations for each spectrum every 15 s) were obtained for each sample. The intensities of the product ion peaks were determined using the WIN-IMS (V4.1) program (BRUKER).

2.2. Identification of product ions using APPI–IMS–MS

To analyze product ions formed by PI, the ion mobility spectrometer–mass spectrometer coupling (IMS–MS) was used. A simplified drift tube with stainless steel drift rings and Teflon insulating rings was attached to an API-III tandem quadrupole mass spectrometer (PE-SCIEX, Toronto, Canada). Coupling these techniques usually entails adjusting the operational parameters of the ion mobility spectrometer due to the small ion flux that can be transferred to the mass spectrometer and the necessary compatibility of the electric fields between the two devices. For these reasons, the measurements were taken with an open shutter and a higher concentration range of compounds than used for IMS alone.

A krypton lamp providing 10 eV and 10.6 eV photons was used as the radiation source for PI source in the IMS. The gaseous samples were introduced via permeation tubes as described previously [16]. The ionization source works at ambient temperature and ambient moisture. Nitrogen was used as drift gas (110 mL/min) and carrier gas (110 mL/min). The ions formed were transferred to the drift tube via the open shutter grid. The drift tube consists of five drift rings 0.95 cm apart. The potential measured at the first ring was +2180 V. The end of the drift tube was fitted into a ceramic socket placed into the high voltage flange of the API-III. The last ring was floated at +280 V and the interface plate for the mass spectrometer was at +90 V enabling the facile transfer of ions to the mass spectrometer. The mass spectrometer used works with a curtain gas flow of 0.6 L/min (nitrogen) for protection of the vacuum system.

Due to the low ion intensity, each mass spectrum was obtained by the accumulation of 50 scans over the mass range of 10–500 amu.

3. Results and discussion

3.1. Ion mobility measurements

The positive ion mobility spectra were obtained using PI and CD ionization. ^{63}Ni ionization was not employed since it provided only weak intensities of peaks due to the low proton affinities of the hydrocarbons investigated. A detailed list of the compounds investigated is shown in Table 1. Ionization energies are only available for mixtures of isomers. The ionization energies of all the compounds are below 10 eV, which permits direct ionization with the krypton lamp. The relative intensities of the peaks in the mobility spectra were not significantly affected by analyte concentration.

The ion mobility spectra of the constitutional monocyclic terpenes (isomers of limonene and terpinene with a molecular

Table 1
Mass spectra and ionization energies of compounds investigated

Substance	*m*/*z*	Mass spectrum (EI: 70 eV), *m*/*z* (relative abundance [%])	Ionization energy (eV)
R(+)-limonene $C_{10}H_{16}$	136	**68** (100), 93 (60), 107 (15), 121 (20), 136 (20)	8.30
S(−)-limonene $C_{10}H_{16}$	136	**68** (100), 79 (20), 93 (45), 107 (15), 121 (15), 136 (15)	
Alpha-terpinene $C_{10}H_{16}$	136	77 (35), 93 (85), **121** (100), 136 (45)	n.a.
Gamma-terpinene $C_{10}H_{16}$	136	77 (30), **93** (100), 121 (30), 136 (35)	
(1*R*)-(+)-*cis*-Pinane $C_{10}H_{18}$	138	***55** (100), 67 (85), 69 (48), 81 (70), 82 (65), 95 (90), 123 (25), 138 (5)	n.a.
(1*S*)-(−)-*cis*-Pinane $C_{10}H_{18}$	138	***55** (100), 67 (83), 69 (50), 81 (65), 82 (65), 95 (78), 123 (20), 138 (4)	
(1*R*)-(+)-*trans*-Pinane $C_{10}H_{18}$	138	***55** (100), 67 (77), 69 (46), 81 (66), 83 (64), 95 (76), 123 (23), 138 (5)	
(1*S*)-(−)-*trans*-Pinane $C_{10}H_{18}$	138	***55** (100), 67 (74), 69 (46), 81 (61), 83 (60), 95 (68), 123 (18), 138 (4)	
(+)-Alpha-pinene $C_{10}H_{16}$	136	77 (20), **93** (100), 105 (10), 121 (15), 136 (6)	8.07
(−)-Alpha-pinene $C_{10}H_{16}$	136	77 (20), **93** (100), 105 (8), 121 (10), 136 (5)	
(+)-Beta-pinene $C_{10}H_{16}$	136	*77 (36), 79 (36) 91 (42), **93** (100), 121 (30), 136 (23)	8.00
(−)-Beta-pinene $C_{10}H_{16}$	136	41 (40), 69 (35), 79 (20), **93** (100), 121 (10), 136 (10)	

The mass spectra were obtained from http://www.webbook.nist.gov/ or (*) measured using an EM640/S mass spectrometer (BRUKER) with electron impact (EI) ionization (70 eV). n.a.: data not available.

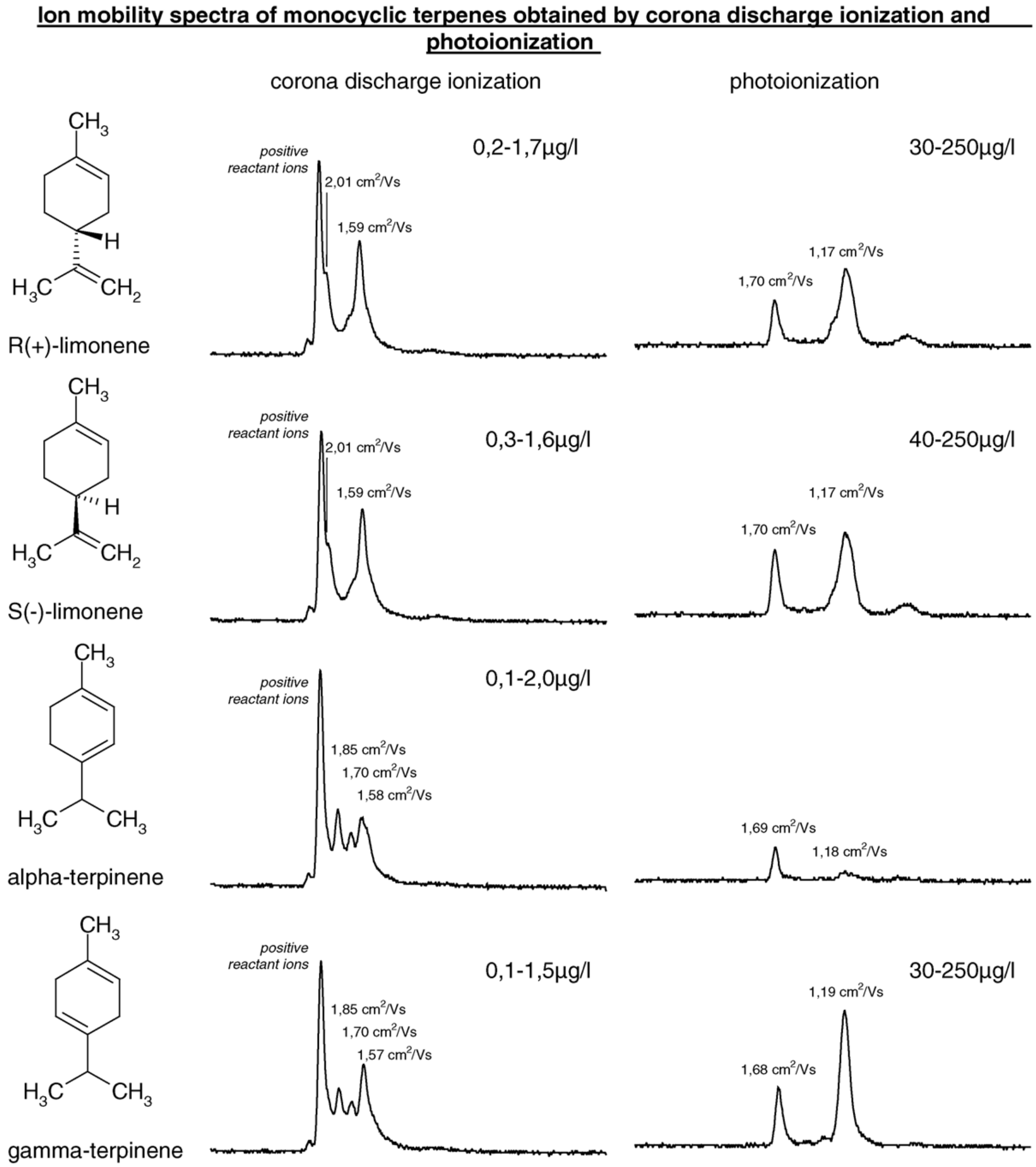

Fig. 1. Ion mobility spectra of monocyclic terpenes.

weight of $m/z = 136$) are shown in Fig. 1. Both double bonds of terpinene are positioned inside the ring while one double bond of limonene is outside. The structures are shown in Fig. 1. As can be seen in this figure, there are some differences in the ion mobility spectra of these substances.

PI provides two major peaks for both limonene enantiomers with K_0 values of 1.70 cm^2/(V s) and 1.17 cm^2/(V s). The relative intensities of these peaks were independent of limonene concentration. Therefore, the ions were not participating in an equilibrium reaction. From past experience, the relative mobilities would suggest that ions of the second peak have approximately twice of the mass of those of the first peak [16]. Therefore, we supposed the formation of ions approximately equal in mass to monomer and dimer ions, i.e., with masses of approximately M and M_2. The comparison of reduced mobility values with those obtained for other hydrocarbons [14,16] indicates that the monomer ions obtained for limonene appear in the drift time range of ion mobility spectra where ions with the molecular weight of limonene can be expected. We will therefore in the following discussion of the IMS spectra refer to the ions as monomer and dimer but with no implication of exact mass or structure. A third peak is present for limonene with a very low intensity. From our past experience, the reduced mobility value associated with this peak is in the range expected for trimeric ions of approximate mass M_3.

CD ionization also provides comparable ion mobility spectra for the enantiomers of limonene. The spectra contain two major peaks with K_0 values of 2.01 $cm^2/(V s)$ and 1.59 $cm^2/(V s)$. Comparison of reduced mobility values with those obtained by PI show that different ions are formed by the two ionization modes. The higher reduced mobility value of the peak at 2.01 $cm^2/(V s)$ indicates a lower ionic mass in comparison with the PI monomer at 1.70 $cm^2/(V s)$. Therefore, we suppose the formation of fragment ions. The peak at 1.59 $cm^2/(V s)$, a value between those of the PI monomer and dimer ions, is assigned to a cluster ion most probably of lower mass than the dimer. This could be the fragment ion associated with the neutral molecule. No ions with the mobility of the monomer 1.70 $cm^2/(V s)$, were observable with CD ionization.

Although the isomers of terpinene and limonene have identical molecular weights and only the positions of the double bonds are different, the ion mobility spectra obtained by CD ionization differ considerably. The spectra of the terpinenes contain three peaks. The peak at 1.70 $cm^2/(V s)$ can be attributed to the monomer ions, which are not detectable for limonene using CD ionization. The reduced mobility value of the cluster ion peak (1.58/7 $cm^2/(V s)$) is comparable with the cluster ion peak obtained for isomers of limonene (1.59 $cm^2/(V s)$). However, there are significant differences in the relative abundances of the ions for the constitutional isomers of terpinene. The reduced mobility values for the fragment ions (1.85 $cm^2/(V s)$ for terpinene) differ between the two compounds (limonene: 2.01 $cm^2/(V s)$). This different fragmentation is known from mass spectrometry using electron impact ionization (Table 1). The base peaks for isomers of terpinene appear at $m/z = 121$ (loss of CH_3) or $m/z = 93$ (loss of C_3H_7). The base peak of the mass spectrum for limonene is at $m/z = 68$ ($C_5H_8^+$ as a result of a retro-Diels–Alder reaction [21]).

PI provides spectra for the isomers of terpinene containing monomer and dimer peaks with K_0 values of 1.68/9 $cm^2/(V s)$ and 1.19/8 $cm^2/(V s)$, respectively, almost identical to those of limonene. However, unlike limonene, the relative intensities of monomer and dimer are very different for the two isomers. Also, in contrast to the isomers of limonene, no trimeric product ions were detected for terpinene. The formation of these ions is evidently affected by the different position of the double bond. Ionic polymerization is possible when the double bond is outside the ring but is less likely due to steric considerations when inside.

CD provides a much more sensitive ionization technique than does PI with an average required concentration range of 0.1–2 μg/L. This is approximately 300 times lower than the 30–250 μg/L required for PI. Neither technique distinguishes between the enantiomers of limonene. Differences in relative abundance of product ions were found for the isomers of terpinene using both ionization techniques. A preferred formation of dimer ions can be observed for gamma-terpinene using PI.

Fig. 2 shows the ion mobility spectra of saturated isomers of pinane. The spectra obtained by PI consist of one main peak, which appears at 1.68/7 $cm^2/(V s)$. Although the molar mass difference from the above-mentioned isomers of limonene and terpinene is only +2 amu, a consistent shift in the reduced mobilities of 0.02/3 $cm^2/(V s)$ is observed.

CD ionization provides at least three peaks in the mobility spectra. The peak at 1.68/9 $cm^2/(V s)$ is comparable with the reduced mobility of the major peak obtained using PI while the peak at 1.85 $cm^2/(V s)$ is comparable to the fragment ion peak detected for the isomers of terpinene. This is in accord with mass spectrometric investigations using electron impact ionization, where the base peak also results from the formation of $C_7H_{11}^+$ ions. Additional cluster ions were found for all isomers of pinane. However, different intensities can be observed for cluster ions in ion mobility spectra obtained by CD ionization. A preferred formation of cluster ions can be established for the enantiomers of *trans*-pinane in comparison with those of *cis*-pinane. Thus, differences were found in the spectra for the diastereomeric compounds (*cis*- and *trans*-pinane).

The results for the isomers of pinene are summarized in Fig. 3. In contrast to the saturated pinanes, PI provides monomer and dimer ions for the unsaturated isomers of alpha-pinene. The peaks at 1.70 $cm^2/(V s)$ and 1.20 $cm^2/(V s)$ can be clearly attributed to such ions. The relative intensities of the monomer and dimer peaks were dependent of concentration, the dimer peak height decreasing relative to that of the monomer as the concentration decreases (Fig. 4).

Trimer ions can be detected for beta-pinene that has a double bond outside the ring. A mass-to-mobility correlation curve was derived from the reduced mobility values obtained by PI. As shown in Fig. 5, an excellent correlation was established between the reduced mobility values and the logarithm of supposed ionic masses. Such a correlation was previously shown for the ions obtained from a set of isomeric hydrocarbon [15].

In accordance with the results shown in Fig. 1 for the monocyclic terpenes, prominent trimeric ions are observed only for compounds with a double bond positioned outside the ring. Furthermore, a higher intensity of dimer ions compared to the monomers can be observed for these compounds. Comparable results were described by Vautz et al. [22] in an investigation of alpha- and beta-pinene and D,L-limonene. Three peaks were found for D,L-limonene and beta-pinene while only two peaks were detected for alpha-pinene using IMS with photoionization.

CD ionization provides similar spectra for isomers of pinene and terpinene. The peak at 1.69 $cm^2/(V s)$ is ascribed to monomer ions. This peak was not observed for limonene. With the exception of limonene, the assumed fragment ions appear at the same reduced mobility (1.85 $cm^2/(V s)$) for all the unsaturated compounds. This is consistent with the

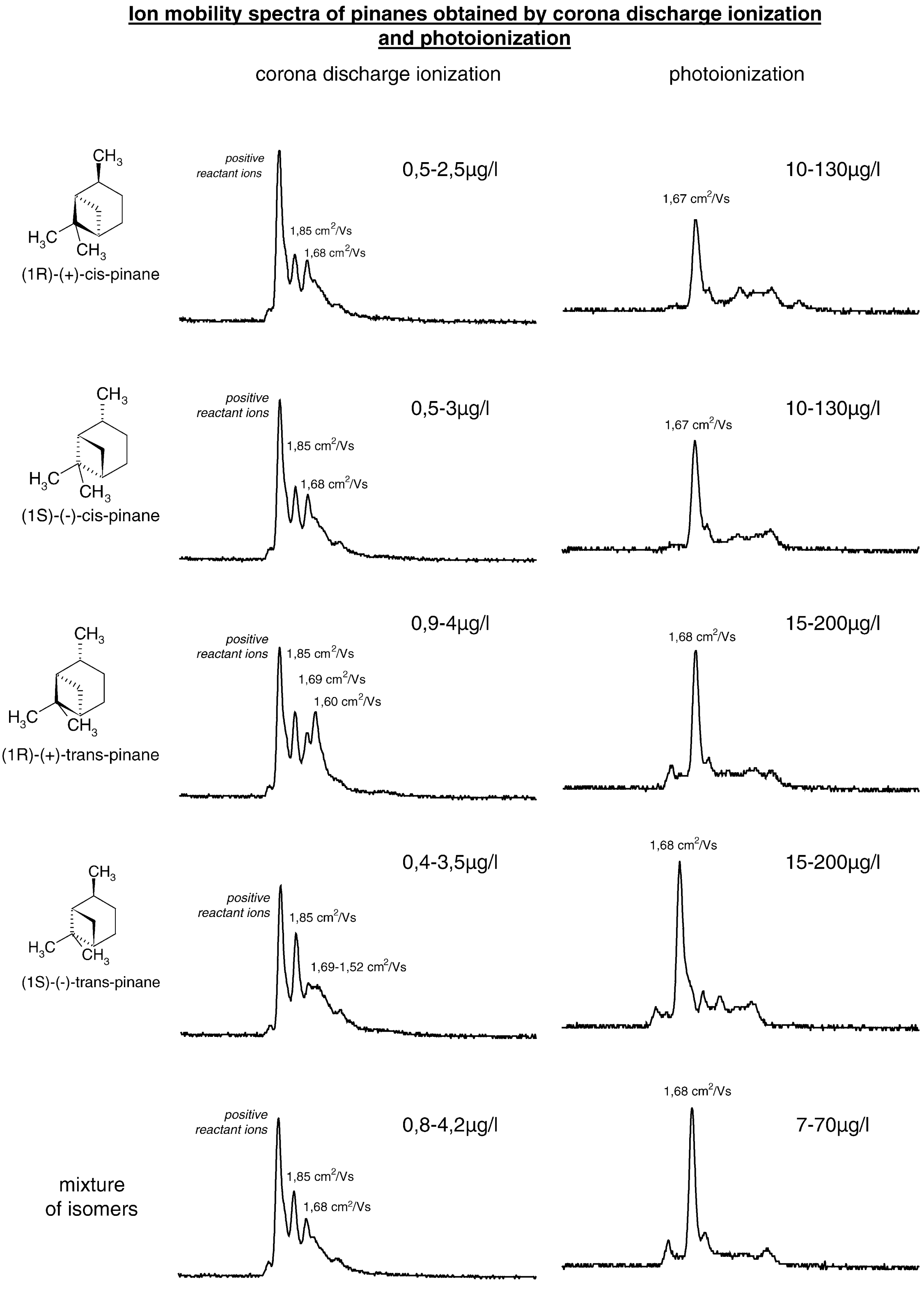

Fig. 2. Ion mobility spectra of bicyclic saturated terpenes.

fragmentation pattern of their electron impact mass spectra (Table 1). Additional cluster ions can be observed for all isomers using CD ionization. However, higher abundances and sharper, more symmetric peak profiles were obtained for alpha-pinene and limonene. The reduced mobility values of these additional peaks are comparable for all substances investigated. Therefore, the formation of similar, but unidentified ions can be assumed.

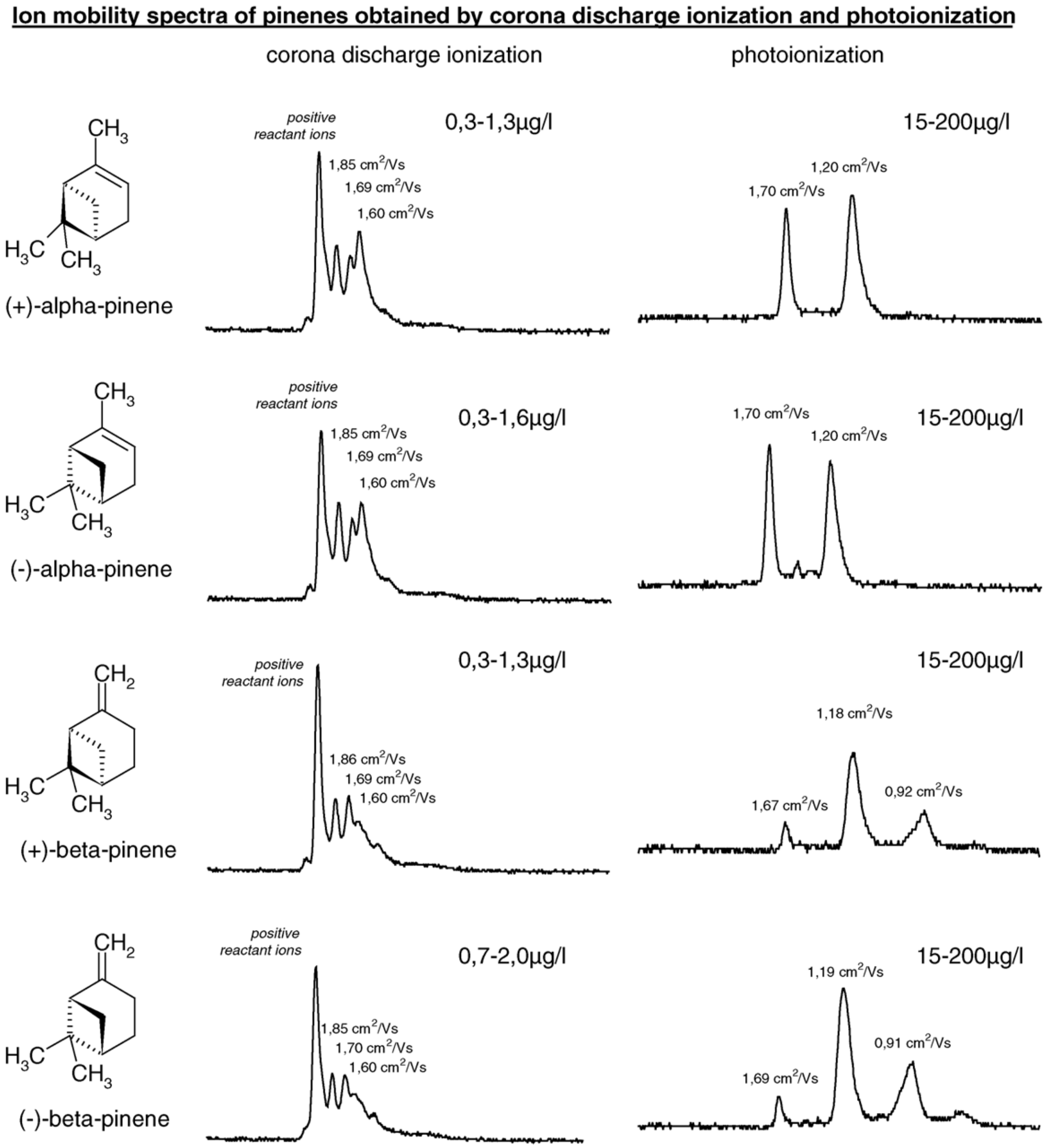

Fig. 3. Ion mobility spectra of isomeric unsaturated bicyclic terpenes.

Obviously, the ionization pathway obtained by CD ionization is partly comparable with that of electron impact mass spectrometry. Besides monomer ions, the typical fragment ions are also observed using mass spectrometry with both electron impact ionization and atmospheric pressure chemical ionization (APCI) using the proton-transfer reaction (PTR)-mass spectrometry [23] and selected ion flow tube (SIFT)-mass spectrometry [17,24] with different reactant gases (using H_3O^+ as reactant gas: $C_{10}H_{17}^+$ and $C_6H_9^+$ product ions and $C_{10}H_{16}^+$ and $C_7H_9^+$ ions using NO^+ for $C_{10}H_{16}$ isomers). CD ionization permits a hundred times more sensitive detection of these compounds in comparison with PI.

The spectra obtained by PI are considerably influenced by the constitution of the compounds (position of double bonds). However, the abundant formation of dimer ions is astonishing for such non-polar compounds using PI. According to the literature [6], M^+ product ions should be expected. Although the IMS investigations indicate the formation of ions as described above, IMS does not permit any definitive mass or structural assignment. The assignment of the ions constituting the IMS peaks as fragment, monomer, dimer and trimer are indicative only of relative masses. PI, that produces ions with little fragmentation, gives confidence that the monomer peak must be due to ions with masses of or close to the molecular mass. Studies of ionization pathways of ter-

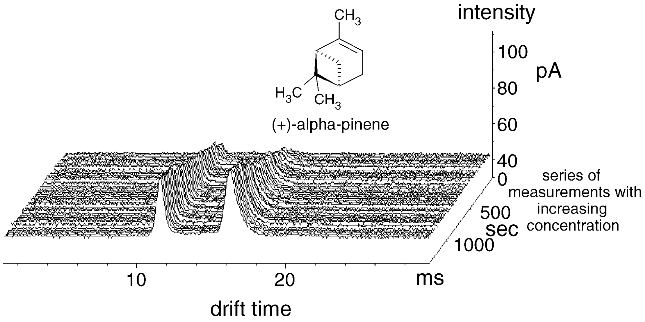

Fig. 4. Correlation between ion mobility spectra and concentration.

penes using PI are not known from the literature. Therefore, mass spectrometric measurements were performed to determine the structure of product ions.

3.2. Peak identification of product ions formed using IMS–MS

Mass spectrometric measurements were performed to determine the *m*/*z* values of ions present in the PI–IMS spectra. In order to obtain a sufficient ion flux in the mass spectrometer it was necessary to both increase the concentration of analyte above that used in obtaining the IMS spectra and also to run with the shutter open. The mass spectra therefore show all ions exiting the mobility spectrometer with no temporal separation. Furthermore, there is always a problem in transferring ions from the high pressure of the mobility spectrometer to the vacuum of the mass spectrometer. Ions, especially weakly bound cluster ions, may be collisionally decomposed in the interface region and adiabatic cooling may encourage ion–neutral association. The ions in the mass spectra may be slightly different to those that would be obtained under IMS ideal conditions.

The used mass spectrometer is cryostatically pumped and has a curtain gas of nitrogen to protect the high vacuum against non-condensable helium present in ambient air. The flow of curtain gas and the potentials of the electrodes in the interface region were optimized to minimize collisional dissociation. No association of the nitrogen curtain gas with any ion was observed. By way of example, Fig. 6 shows the mass spectra obtained for gamma-terpinene under different interface conditions. In Fig. 6(a), ions are passed through the interface with sufficient energy that few ions above *m*/*z* 175 are present. The base peak is that of the molecular ion, *m*/*z* 136, and the lower *m*/*z* ions are the fragment ions in the electron impact mass spectrum shown in Table 1. With the much gentler conditions of Fig. 6(b), the base peak at *m*/*z* 273 and other high mass ions are present and there are essentially no fragment peaks below the molecular ion.

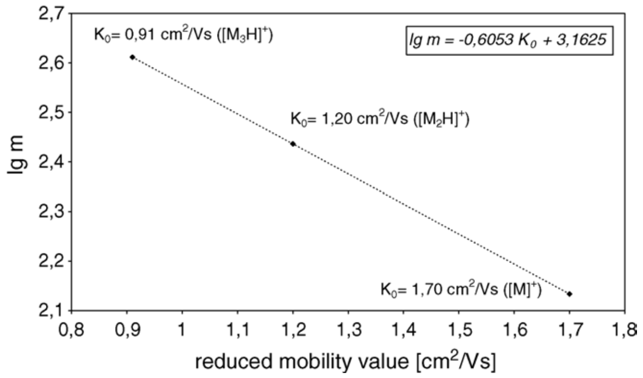

Fig. 5. Mass-to-mobility correlation line for isomers of pinene.

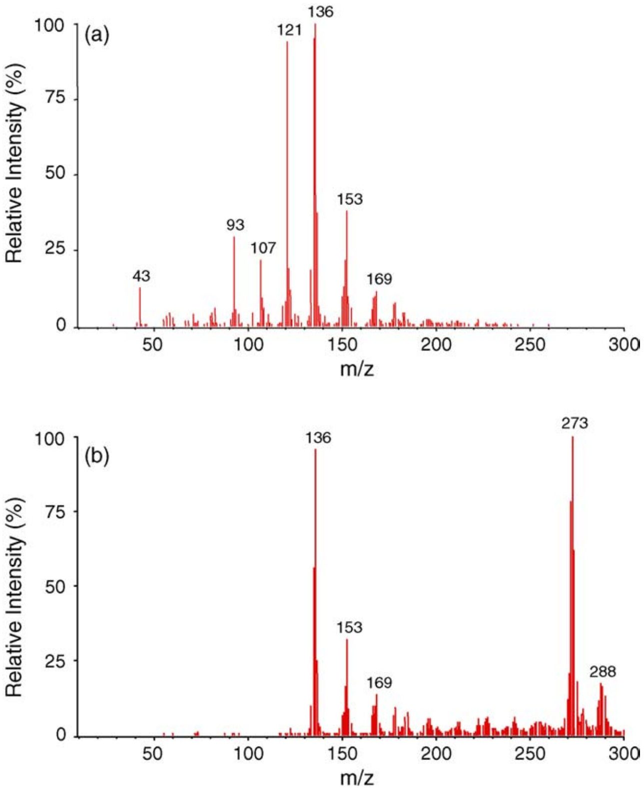

Fig. 6. APCI (PI)–IMS–MS spectra of gamma-terpinene obtained using different experimental conditions: (a) interface plate voltage: 100 V and orifice plate voltage: 60 V; (b) interface plate voltage: 90 V and orifice plate voltage: 40 V.

Alpha- and gamma-terpinene were investigated as examples of constitutional isomers with the double bond inside the ring, (1*R*)-*cis*- and (1*S*)-*trans*-pinane as examples for diastereomers (saturated compounds). Also, *R*-(+)-limonene with double bond outside the ring and (+)-alpha-pinene were studied. The results of mass spectrometric investigations are summarized in Table 2. The mass spectra obtained confirm our conclusions regarding ion mobility measurements using PI.

The base peak of the mass spectrum obtained for *R*-(+)-limonene appears at *m*/*z* 271. This mass can be assigned to $[M(M-1)]^+$. No molecular ions are present at *m*/*z* 136. The peak at *m*/*z* 135 is the $[M-1]^+$ ion. Peaks of low intensity are present just above $[M-1]^+$ with *m*/*z* values 151, 169 and 185. There is a similar pattern of peaks above *m*/*z* 271 with somewhat higher intensities. The mass differences between

Table 2
Results of IMS–MS investigations

Substance	*m*/*z*	PI–IMS–MS, *m*/*z* (relative abundance [%]) of major peaks
R(+)-limonene	136	135 (34), 151 (8), 169 (4), 179 (3), 185 (8), **271** (**100**), 279 (6), 288 (19), 304 (46), 320 (17), 336 (6), 338 (6), 352 (3), 354 (3)
Alpha-terpinene	136	**136** (**100**), 153 (57), 171 (11), 195 (10), 223 (7), 227 (9), 253 (3), 273 (5), 287 (19), 304 (17), 319 (9)
Gamma-terpinene	136	136 (27), 153 (12), 169 (5), **273** (**100**), 279 (8), 288 (17), 305 (31), 321 (42), 337 (10), 347 (10), 352 (4)
(1*R*)-(+)-*cis*-Pinane	138	137 (37), **153** (**100**), 169 (19), 183 (15), 198 (9), 220 (6), 245 (5), 248 (8), 264 (8), 266 (11), 276 (23), 290 (19), 308 (21), 322 (7), 324 (7), 338 (13)
(1*S*)-(−)-*trans*-Pinane	138	**137** (**100**), 153 (38), 167 (10), 169 (13), 183 (11), 197 (6), 211 (6), 226 (9), 240 (4), 249 (5), 255 (7), 266 (10), 276 (8), 282 (9), 290 (15), 306 (26), 323 (5), 341 (3)
(+)-Alpha-pinene	136	135 (30), 151 (6), 153 (6), 169 (3), 251 (3), **272** (**100**), 278 (4), 288 (31), 304 (26), 320 (5)

pairs of peaks in the two sets are similar viz. 288 − 151 = 137; 304 − 169 = 135; 320 − 185 = 135. The higher mass ions are condensation products of lower mass ions that are most certainly accentuated in the IMS–MS spectra because of the necessary use of a higher concentration of analyte. The monomer and dimer peaks in the IMS spectrum shown in Fig. 1 are due to $[M-1]^+$ and $[M(M-1)]^+$. There are no ions around *m*/*z* 410 in the mass spectrum of Fig. 7 showing that the trimer observed in the IMS spectrum did not survive passage through the IMS–MS interface.

The breakdown diagram for photoionized *R*-(+)-limonene has been determined from 8.5 eV to 10.6 eV using synchrotron irradiation [26]. At 10.0 eV, appropriate to krypton radiation, the molecular ion comprises approximately 50% of total ionization with fragment ions decreasing in intensity in the order: *m*/*z* 94, *m*/*z* 121, *m*/*z* 107 and *m*/*z* 79. None of these ions is seen in the mass spectrum of Fig. 7, all must have disappeared by ion molecule reaction. The fragment ions probably reacted by hydride abstraction from the parent molecule to give the $[M-1]^+$ ion but the fate of the molecular ion is not obvious [25].

The mass spectra obtained with *R*-(+)-limonene and five of the other compounds are summarized in Table 2. The pattern shown by all the unsaturated compounds is similar to that shown by *R*-(+)-limonene, i.e., a monomer and dimer peak with a series of ions at higher mass following each peak. Taking into account the higher concentrations used in the IMS–MS study, the results confirm the IMS results. For example, gamma-terpinene has a base peak at *m*/*z* 273 consistent with the large dimer peak in the mobility spectrum while for alpha-terpinene the base peak is at *m*/*z* 136, consistent with the dominant monomer peak in the mobility spectrum. *m*/*z* 136 is the molecular ion for terpinene while *m*/*z* 273 corresponds to M_2H^+. In confirmation of the mobility results that found no evidence that the dimer and monomer ions were in an equilibrium situation, these M^+ and M_2H^+ ions cannot be linked by an equilibrium reaction. Photoionization of the two terpinenes does not therefore lead to a common ion structure, and the conjugated isomer shows fewer tendencies for further ion–molecule reactions. It is also notable that, apart from *m*/*z* 153, the ions in the series above the monomer and dimer are not the same for the two isomers, differences of one or two mass units being evident.

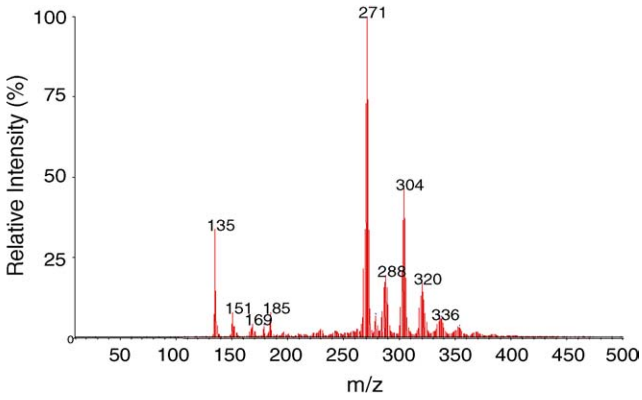

Fig. 7. PI–IMS–MS spectrum of *R*-(+)-limonene.

The mass spectra of (1*R*)-(+)-*cis*- and (1*S*)-(−)-*trans*-pinane, like the mobility spectra, have the largest peak in the low mass region and show no major peak in the dimer region. Both have an $[M-1]^+$ peak which is the base peak for the *trans* isomer but is only 37% of the base peak (*m*/*z* 153) of the *cis* isomer for which $[M+15]^+$ is the major ion. This ion is 38% of the base peak for the *trans* isomer. This disparity between the isomers is inconsistent with the IMS results that show almost identical mobility coefficients for the largest peak in each spectrum. It may simply be due to a difference in sample concentration between the two mass spectrometric results, which could not be as carefully controlled and were considerably higher than in the IMS study.

(+)-Alpha-pinene, that shows two prominent and well resolved monomer and dimer peaks in the mobility spectrum, also shows comparable prominent peaks in its mass spectrum. The base peak at *m*/*z* 272 corresponds to $M_2{}^+$, while the $[M-1]^+$ peak at *m*/*z* 135 is 30% of the base peak intensity. It is interesting that of all the compounds in Table 2 (+)-alpha-pinene is the only one that yields an $M_2{}^+$ ion. It must be formed by the association of the initially formed molecular ion with the neutral molecule but whether or not the molecular ion is an opened ring structure and why limonene, for example, does not show the same dimer structure are unanswered questions.

As can be seen from these results, there is a correspondence between ions surmised to be present in the mobility spectra and those found in the IMS–MS investigations. A compound with a large dimer peak in its mobility spectrum also showed a prominent ion at approximately twice the molar mass in its mass spectrum. As was also found in the IMS study, none of the monomer and dimer ions, with the exception of those of *R*-(+)-limonene, differ exactly in mass by the molar mass of the compound, i.e., the dimers are not simply monomers solvated by the parent molecule. The differences are very close to the molar mass but there is no equilibrium between any one of the pairs.

4. Conclusion

The constitutional isomers investigated in this study differ in the position of the double bonds. Differences in this structural feature provide differences in ion mobility spectra as described above and permit the distinction between these constitutional isomers. Using PI, the abundant formation of dimer and trimeric product ions can be established for substances with a double bond outside the carbon ring in comparison to compounds with the double bond inside the ring. Different fragmentation patterns were found in ion mobility spectra obtained by IMS with CD ionization for these substances.

Only small differences in ion mobility spectra can be observed for the diastereomers investigated. There are differences in the abundance of cluster ions formed by CD ionization. Nearly identical spectra can be observed using PI.

As expected, the enantiomers analyzed in this study exhibit identical spectra.

Although the ion mobility spectra obtained using common spectrometers cannot be completely reproduced with the IMS–MS experiments, the general structures of product ions formed can still be assigned. The product ions formed by IMS can be clearly attributed to the structures identified using IMS–MS. Using APCI (PI)–IMS–MS, ions with ions with similar masses as expected from IMS measurements were mainly formed for nearly all isomers investigated. Differences in ion formation between the separate isomers can be concluded from the mass spectra obtained as well as ion mobility spectra.

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