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Electron impact ionization of acetaldehyde

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ABSTRACT

An electron impact (EI) ion source and a double focusing sector field mass spectrometer were used to investigate ionization processes of acetaldehyde C_2H_4O. The ionization and appearance energies for observed single $C_xH_yO_z^+$ ($x = 0, 1, 2$; $y = 0, 1, \ldots, 4$; $z = 0, 1$) and double $C_2H_2O^{2+}$ charged ions have been determined by using the non-linear least-square fitting procedure to the raising set of the data points. In the case of ions C_2HO^+, C_2O^+, CH_3O^+, CH_2O^+, $C_2H_2^+$, C_2H^+, C_2^+, H_2O^+, HO^+ and $C_2H_2O^{2+}$ the appearance energies were obtained for the first time.

1. Introduction

Acetaldehyde C_2H_4O is very important molecule from the scientific and applied points of view. It occurs naturally in ripe fruit, coffee and fresh bread and is produced by plants as a part of their natural metabolism. This molecule is an air pollutant resulting from combustion, such as automotive exhaust fumes and tobacco smoke, contributing to the addictive properties of tobacco [1,2]. Investigation of ionization processes of acetaldehyde is being a subject of studies of many investigators within last few decades. For these investigations, and especially for determination of appearance energies of acetaldehyde fragment ions several measurement techniques were applied (EI, electron impact; PI, photoionization; PE, photoelectron spectroscopy; S, optical spectroscopy; PIPECO, photoion–photoelectron coincidence spectroscopy). Most of them concern the ionization energy of pattern ion $C_2H_4O^+$. For the wide spectrum of observed fragment ions created during the fragmentation in the ion source not every values of appearance potentials are reported.

In our laboratory observations of metastable fragmentation reactions of ions produced by electron impact of molecules play a special role [3–9]. Just absence of metastable fragmentation reactions of acetaldehyde ions was for us direct encouragement for the investigations presented here.

Therefore, in this work mass spectrometric investigations of ionization or appearance energies for all observed acetaldehyde ions produced by electron impact are presented. To our knowledge, this is the first time that threshold and appearance energies for all observed ions from electron impact of acetaldehyde have been measured on the apparatus using the same method.

2. Experimental

A high-resolution double focusing sector field mass spectrometer of reversed Nier–Johnson-type B–E geometry with the Nier-type electron impact ion source was applied for investigations presented here (Fig. 1). This spectrometer is an improved version of the MX 1321-type spectrometer used by us for investigations of ionization processes in gasses and gaseous clusters and was described in detail previously [10–12]. This apparatus is equipped with a channeltron-

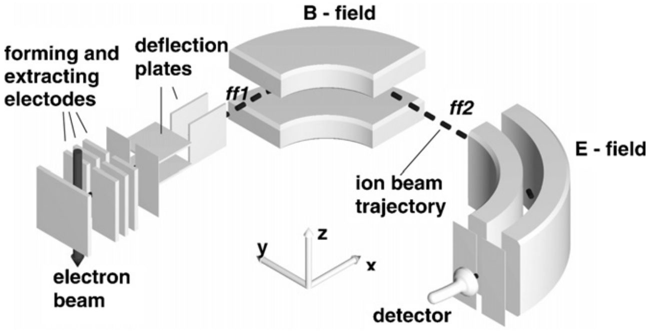

Fig. 1. Schematic view of the double focusing sector field mass spectrometer of reversed Nier–Johnson-type B–E geometry.

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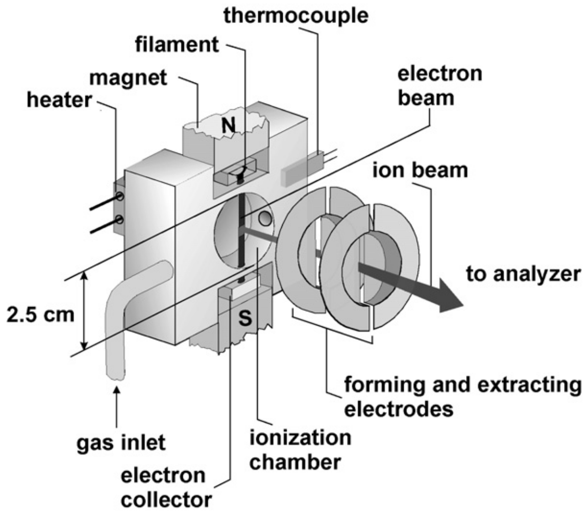

Fig. 2. The electron impact ion source.

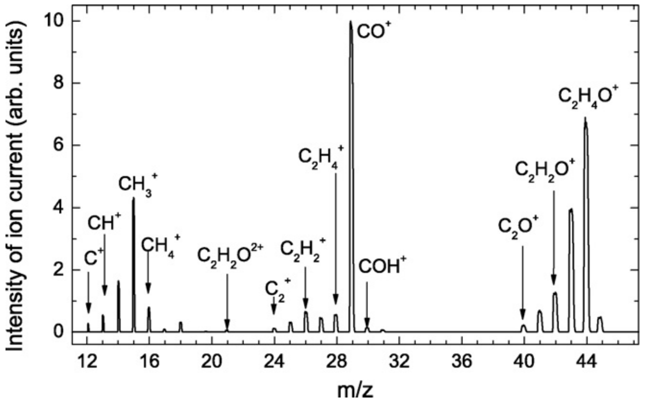

Fig. 3. Electron impact mass spectrum of acetaldehyde. The electron ionization energy E_e = 100 eV and the intensity of electron beam I_e = 0.3 mA.

type-based detection system and the vacuum system allows to work with a background pressure of 4×10^{-8} mbar.

The schematic view of electron impact ion source is presented in Fig. 2. In the ionization chamber a magnetic field (magnet) is parallel to the electron beam axis. The electron energy is scanned in an automated stepwise mode with the energy increment of 0.1 eV starting from 0 up to 100 eV. In the present experiment the electron beam current was set up to 0.3 mA. The maximum electron current can be set up to 1.0 mA. The ion source pressure is controlled by a Balzers Compact Full Range

Table 1
Ionization and appearance energies

Ion	Other products	Ionization or appearance energies (eV)		
		This work	Method	Literature
$C_2H_4O^+$		10.20 ± 0.1	EI	10.23 [33]; 10.14 ± 0.02 [34]
			PI	10.20 ± 0.03 [19]; 10.21 ± 0.01 [20]; 10.25 ± 0.03 [21]; 10.20 ± 0.03 [22]; 10.22 ± 0.01 [23]; 10.20 ± 0.02 [24]; 10.22 ± 0.01 [25]; 10.20 ± 0.02 [26]; 10.22 ± 0.01 [27]; 10.2298 ± 0.0007 [28]; 10.20 [29]; 10.22 [30]; 10.22 [31]; 10.22 [32]
			PE	10.20 [35]; 10.22 ± 0.01 [36]; 10.24 ± 0.02 [37]; 10.21 [38]; 10.26 [39]; 10.20 [40]; 10.9 [41]; 10.20 [42]; 10.227 ± 0.005 [43]; 10.23 [44]; 10.3 [45]
			S	10.2291 ± 0.0007 [17]; 10.19 [18]
			PIPECO	10.24 [46]
$C_2H_3O^+$	H	11.00 ± 0.1	EI	10.5 ± 0.2 [47]; 10.75 ± 0.08 [48]; 11.0 ± 0.1 [50]; 10.67 [31];
			PI	10.89 [23]; 10.89 ± 0.03 [25]; 10.90 ± 0.03 [27]; 10.82 ± 0.03 [26]; 10.82 [29]; 10.90 [30]
			PIPECO	10.50 ± 0.05 [49]
$C_2H_2O^+$	H_2	12.70 ± 0.1	EI	10.7 ± 0.1 [23]
			PI	13.06 ± 0.09 [27]
C_2HO^+	H_3	14.20 ± 0.1	EI	
C_2O^+	H_2H_2	13.50 ± 0.2	EI	
CH_3O^+	CH	13.50 ± 0.2	EI	
CH_2O^+	CH_2	11.80 ± 0.2	EI	
CHO^+	CH_3	12.20 ± 0.1	EI	
			PI	11.78 [32]; 11.79 ± 0.03 [26]; 11.79 ± 0.03 [24]
$CO^+/C_2H_4{}^+$	CH_4/O	11.90 ± 0.15	EI	13.9 ± 0.1 [47]; 14.0 ± 0.1 [47];
$C_2H_3{}^+$	OH	15.60 ± 0.2	EI	14.17 ± 0.13 [27];
$C_2H_2{}^+$	HOH	15.40 ± 0.2	EI	
C_2H^+	H_2+OH	22.70 ± 0.2	EI	
$C_2{}^+$	H_2+HOH	32.00 ± 0.2	EI	
$C_2H_2O^{2+}$	H_2	29.30 ± 0.4	EI	
HOH^+	C_2H_2	10.90 ± 0.2	EI	
HO^+	C_2H_3	10.60 ± 0.2	EI	
$CH_4{}^+/O^+$	CO/C_2H_4	12.80 ± 0.1	EI	
			PI	12.61 ± 0.06 [27]; 12.61 [30]
$CH_3{}^+$	CHO	13.30 ± 0.1	EI	14.53 [51];
			PI	14.11 ± 0.05 [26]; 14.08 ± 0.05 [27]; 14.08 [30]
			PIPECO	13.9 ± 0.1 [49]
$CH_2{}^+$	CH_2O	18.50 ± 0.1	EI	
			PI	15.08 ± 0.09 [27]
CH^+	C_2H_3O	20.60 ± 0.1	EI	
C^+	CH_4O	21.40 ± 0.2	EI	

EI, electron impact; PI, photoionization; PE, photoelectron spectroscopy; S, optical spectroscopy; PIPECO, photoion–photoelectron coincidence spectroscopy.

Gauge PKR 250 placed near the ionization chamber. The temperature of ionization chamber is controlled by the alumel–chromel thermocouple and is about 500 K at the typical working conditions.

In the present experiment liquid acetaldehyde (purity 99.5%, purchased from Sigma–Aldrich) is kept at temperature, 310 K and the vapor of it is introduced via a capillary leak gas inlet system into the collision chamber of the ion source. Neutral gas target under the pressure of 6×10^{-7} mbar is crossed by a well-characterized magnetically collimated electron beam with FWHM energy spread of ~0.5 eV. For this pressure the calculated mean free path for C_2H_4O/C_2H_4O collisions in the ionization chamber is higher than 300 m and it means that typical ion/molecule reactions are negligible from a practical point of view. For this pressure the fast internal ion/molecule half reactions can take place [13–16].

The ion accelerating voltage can be changed from 0 up to 6 kV depending on the experimental purposes and in general is set to 4 kV. Ensuing cations are extracted by a weak electric field, pass through the system of the ion beam forming lenses (focusing and deflecting) and finally are accelerated to the mass spectrometer through a potential drop of $U_{acc} = 4$ kV. They pass through a narrow entrance slit and the first field-free region (ff_1, length 15 cm),

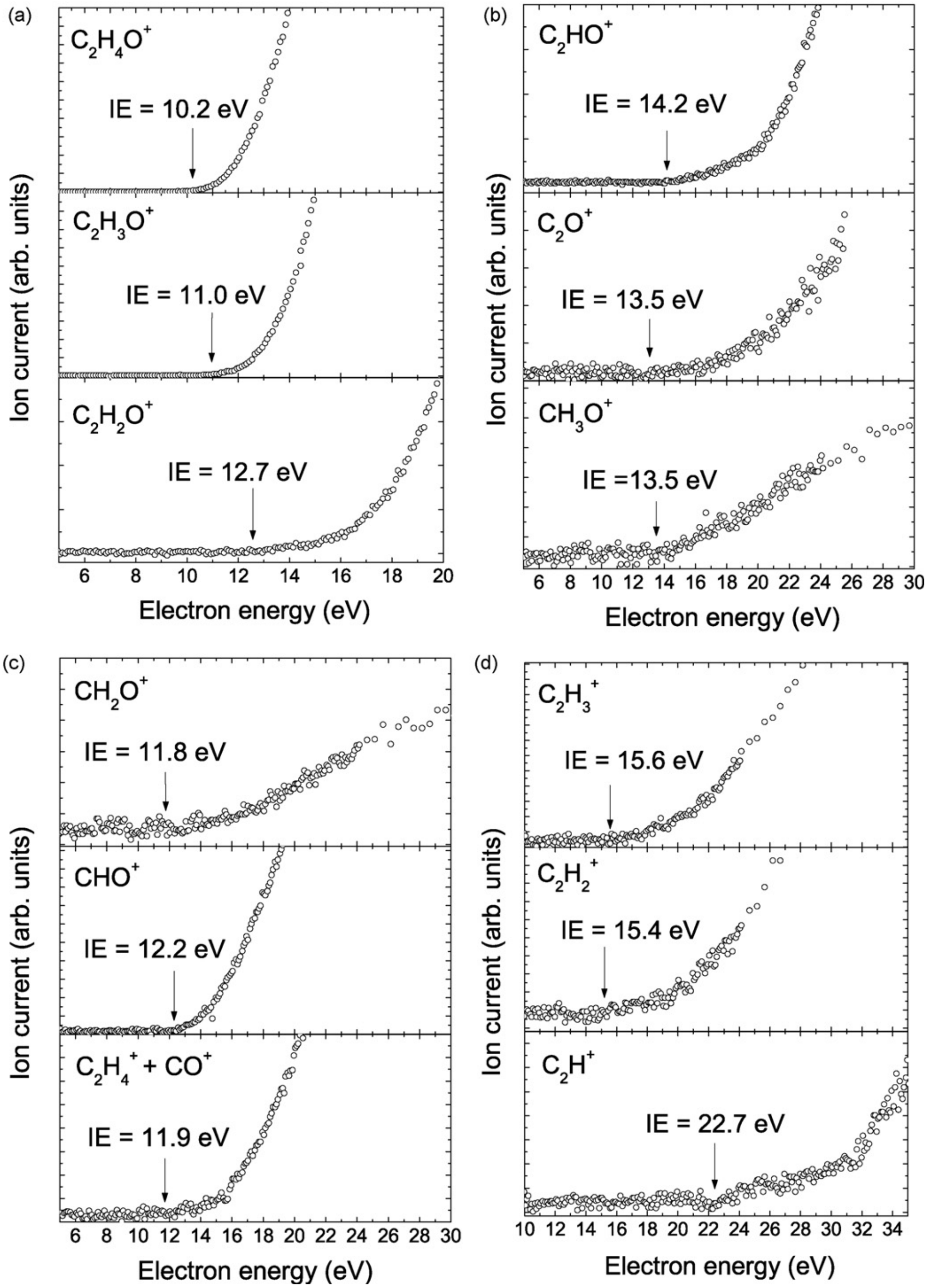

Fig. 4. Intensity of ion current as a function of the electron energy at the intensity of the electron beam $I_e = 0.3$ mA: (a) $C_2H_4O^+$, $C_2H_3O^+$, $C_2H_2O^+$; (b) C_2HO^+, C_2O^+, COH_2^+; (c) CH_2O^+, COH^+, $C_2H_4^+$ and CO^+; (d) $C_2H_3^+$, $C_2H_2^+$, C_2H^+; (e) C_2^+, $C_2H_2O^{2+}$, HOH^+; (f) OH^+, CH_4^+ and O^+, CH_3^+; (g) CH_2^+, CH^+, C^+.

are momentum-analyzed by a 90° magnetic sector field B (radius 15 cm), enter the second field-free region (ff_2, length 40 cm), pass through a 90° electric sector field E (radius 24 cm) and finally are detected by a channeltron-type electron multiplier.

3. Results

In all measurements described here, the temperature of ionization chamber has the established value of about 500 K. The typical electron impact mass spectrum of acetaldehyde taken at 100 eV electron energy is shown in Fig. 3. Ions originating from the residual gas in the background (4×10^{-8} mbar) were substracted by mass spectra that were measured without acetaldehyde in the gas inlet system. For electron impact ionization of acetaldehyde C_2H_4O the following reactions can take place:

$$e + C_2H_4O \rightarrow C_xH_yO_z{}^+ + 2e \quad \text{(singleionization)} \tag{1a}$$

$$e + C_2H_4O \rightarrow C_2H_2O^{2+} + H_2 + 3e \quad \text{(doubleionization)} \tag{1b}$$

where $x = 0, 1, 2$; $y = 0, 1, \ldots, 4$; $z = 0, 1$.

The mass spectrum of the acetaldehyde clearly reveals the presence of double charged ions at the mass to charge ratio $m/z = 21$ resulting from $C_2H_2O^{2+}$ (reaction 1b).

For all observed ions ionization or appearance energies were determined and results of our measurements are presented in Fig. 4. Electron energy scale was calibrated against the well-known threshold for the Ar atom. For these calibrations the accuracy is not worse than ±0.5 eV. These energies have been determined by using the non-linear least-square fitting procedure to the raising set of data points. A good enough agreement between our measurement and the others for ionization energy of pattern ion $C_2H_4O^+$ encouraged us to undertake a similar study (appearance potentials) for all the observed ions. Our results of ionization and appearance energies and results obtained by the other authors who used different experimental methods are collected in Table 1.

4. Conclusion

An electron impact (EI) ion source on a double focusing sector field mass spectrometer was used to investigate ionization and appearance energies for observed single $C_xH_yO_z{}^+$ ($x = 0, 1, 2$, $y = 0, 1, \ldots, 4$; $z = 0, 1$) and double $C_2H_2O^{2+}$ charged ions from acetaldehyde. These energies have been determined by using the non-linear least-square fitting procedure. For the ions C_2HO^+, C_2O^+, CH_3O^+, CH_2O^+, $C_2H_2{}^+$, C_2H^+, $C_2{}^+$, H_2O^+, HO^+ and $C_2H_2O^{2+}$ these results are presented for the first time up to our knowledge.

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References

[1] C. Berhens, L.A. Paquette, Org. Synth.: Colloids 10 (2004) 41.
[2] Q. Xiao, H. Weiner, D.W. Crabb, J. Clin. Invest. 98 (9) (1996) 2027.
[3] K. Gluch, J. Fedor, S. Matt-Leubner, O. Echt, A. Stamatovic, M. Probst, P. Scheier, T.D. Märk, J. Chem. Phys. 118 (2003) 3090.
[4] K. Gluch, S. Matt-Leubner, O. Echt, R. Deng, J.U. Andersen, P. Scheier, T.D. Märk, Chem. Phys. Lett. 385 (2004) 449.
[5] K. Gluch, S. Matt-Leubner, O. Echt, B. Concina, P. Scheier, T.D. Märk, J. Chem. Phys. 121 (2004) 2137.
[6] K. Gluch, S. Matt-Leubner, L. Michalak, O. Echt, A. Stamatovic, P. Scheier, T.D. Märk, J. Chem. Phys. 120 (2004) 2686.
[7] S. Feil, O. Echt, K. Gluch, V.G. Hasan, S. Matt-Leubner, T. Tepnual, V. Grill, A. Bacher, P. Scheler, T.D. Märk, Chem. Phys. Lett. 411 (2005) 366.
[8] K. Gluch, S. Feil, V.G. Hasan, S. Matt-Leubner, T. Tepnual, O. Echt, V. Grill, P. Scheier, T.D. Märk, Vacuum 78 (2005) 187.
[9] K. Głuch, J. Cytawa, L. Michalak, Kinetic energy release of metastable ions produced from C_3H_3N, Vacuum, submitted for publication.
[10] L. Michalak, A. Pelc, Vacuum 52 (1999) 261.
[11] A. Pelc, L. Michalak, Rapid Commun. Mass Spectrom. 14 (16) (2000) 1455.
[12] A. Pelc, L. Michalak, Int. J. Mass Spectrom. Ion Process. 194 (1) (2000) 85.
[13] G. Romanowski, K.P. Wanczek, Int. J. Mass Spectrom. Ion Process. 62 (1984) 277.
[14] A. Stamotovic, K. Stephan, T.D. Märk, Int. J. Mass Spectrom. Ion Process. 63 (1985) 37.
[15] H. Shinohara, N. Nishi, N. Washida, J. Chem. Phys. 83 (1985) 1939.
[16] H. Haberland, H.Z. Langosch, Phys. D 2 (1986) 243.
[17] A.D. Walsh, Proc. R. Soc. (Lond.) A 185 (1946) 176.
[18] H. Ogata, J. Kitayama, M. Koto, S. Kojima, Y. Nihei, H. Kamada, Bull. Chem. Soc. Jpn. 47 (1974) 958.
[19] F.I. Vilesov, A.N. Terenin, Dokl. Akad. Nauk SSSR 115 (1957) 539 (in Russian).
[20] K. Watanabe, J. Chem. Phys. 26 (1957) 542.
[21] H. Hurzeler, M.G. Inghram, J.D. Morrison, J. Chem. Phys. 28 (1958) 76.
[22] I. Vilesov, Dokl. Phys. Chem. 132 (1960) 1332 (in Russian).
[23] V.K. Potapov, A.D. Filyugina, D.N. Shigorin, G.A. Ozerova, Dokl. Akad. Nauk SSSR 180 (1968) 352 (in Russian).
[24] C.S. Matthews, P. Warneck, J. Chem. Phys. 5 (1969) 854.
[25] V.K. Potapov, V.K. Sorokin, Khim. Vys. Energ. 6 (1972) 387 (in Russian).
[26] P. Warneck, Z. Naturforsch. A 29 (1974) 350.
[27] R. Krassig, D. Reinke, H. Baumgartel, Ber. Bunsen-Ges. Phys. Chem. 78 (1974) 425.
[28] D.J. Knowles, A.J.C. Nicholson, J. Chem. Phys. 60 (1974) 1180.
[29] R.H. Staley, R.D. Wieting, J.L. Beauchamp, J. Am. Chem. Soc. 99 (1977) 5964.
[30] H.W. Jochims, W. Lohr, H. Baumgartel, Chem. Phys. Lett. 54 (1978) 594.
[31] J.C. Traeger, R.G. McLouglin, A.J.C. Nicholson, J. Am. Chem. Soc. 104 (1982) 5318.
[32] J.C. Traeger, Int. J. Mass Spectrom. Ion Process. 66 (1985) 271.
[33] J.L. Holmes, J.K. Terlouw, F.P. Lossing, J. Phys. Chem. 80 (1976) 2860.
[34] T.M. El-Sherbini, S.H. Allam, M.D. Migahed, A.M. Dawoud, Z. Naturforsch. A 36 (1981) 1334.
[35] M.J.S. Dewar, S.D. Worley, J. Chem. Phys. 50 (1969) 654.
[36] B.J. Cocksey, J.H.D. Eland, C.J. Danby, J. Chem. Soc., B (1971) 790.
[37] D. Chadwick, A. Katrib, J. Electron Spectrosc. Relat. Phenom. 3 (1974) 39.
[38] W.C. Tam, D. Yee, C.E. Brion, J. Electron Spectrosc. Relat. Phenom. 4 (1974) 77.
[39] K. Kimura, S. Katsumata, T. Yamazaki, H. Wakabayashi, J. Electron Spectrosc. Relat. Phenom. 6 (1975) 41.
[40] J.L. Meeks, J.F. Arnett, D. Larson, S.P. McGlynn, Chem. Phys. Lett. 30 (1975) 190.
[41] C.N.R. Rao, Indian J. Chem. 13 (1975) 950.
[42] S.P. McGlynn, J.L. Meeks, J. Electron Spectrosc. Relat. Phenom. 6 (1975) 269.
[43] R. Hernandez, P. Masclet, G. Mouvier, J. Electron Spectrosc. Relat. Phenom. 10 (1977) 333.
[44] F.M. Benoit, A.G. Harrison, J. Am. Chem. Soc. 99 (1977) 3980.
[45] G. Bieri, L. Asbrink, W. Von Niessen, J. Electron Spectrosc. Relat. Phenom. 27 (1982) 129.
[46] K. Johnson, I. Powis, C.J. Danby, Chem. Phys. 70 (1982) 329.
[47] F.H. Dorman, J. Chem. Phys. 42 (1965) 65.
[48] D.N. Shigorin, A.D. Filyugina, V.K. Potapov, Teor. i Eksperim. Khim. 2 (1966) 417 (in Russian).
[49] R. Bombach, J.P. Stadelmann, J. Vogt, Chem. Phys. 60 (1981) 293.
[50] P.C. Burgers, J.L. Holmes, Org. Mass Spectrom. 17 (1982) 123.
[51] M.A. Haney, J.L. Franklin, J. Chem. Soc., Faraday Trans. 65 (1969) 1794.