

Reviews

Resonant electron capture negative ion mass spectrometry: the state of the art and the potential for solving analytical problems

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Resonant electron capture negative ion mass spectrometry (REC NI MS) is a highly informative method of investigation of low-energy electron-molecule reactions, thermochemistry, and kinetics of negative ion formation and decay. The review includes consideration of the physical principles and specific features of the method, a brief historical survey, terminological issues, and an outline of instrumentation. The potential of REC NI MS for solving structural and analytical problems is analyzed and the advantages of the method over classical positive ion MS are demonstrated. The results of analytical studies of organic and organoelement compounds using various types of mass spectrometers are reviewed. The reasons for low adoption of REC NI MS are analyzed and arguments are presented in favor of introducing the method into analytical practice as an additional tool implemented on the available instruments. Prospects for the development and improvement of REC NI MS for solving unconventional problems are discussed.

Key words: resonant electron capture negative ion mass spectrometry, methods of analytical chemistry, positive ions, electron autodetachment, ionization, fragmentation, GC/MS, analytical instrumentation.

Introduction

Human activity in many areas including medicine and biology, as well as chemical, food, and pharmaceutical industries, forensics, drug control, doping control, industrial and environmental monitoring, and counter-terrorist security involves the detection, identification and

quantification of the composition of complex mixtures of chemical compounds. Continuous complication of these topical problems imposes heightened requirements for the reliability, informativity, sensitivity, versatility, operation speed, and cost of solution methods. All these requirements are best met by mass spectrometry (MS), a method for comprehensive investigation of various physicochemical

processes in gases and condensed media. However, the main field of practical application of MS is the determination of chemical composition of various substances.¹

Discussing mass spectrometry as a widely used method implies positive ion MS (PI MS), which has strong scientific, methodological, and technological basis and allows one to study a wide range of targets. Negative ion mass spectrometry (NI MS) is much less widespread, still being considered as an exotic experimental method. Although the first idea of NI MS dates back to the works of J. J. Thomson who coined^{2,3} to use crossed electric and magnetic fields to determine the mass-to-charge (m/z) ratios of PI and NI, its progress was delayed for five decades^{4–7} due to specific features of the method. These include the resonant nature of NI (*cf.* threshold nature of PI), small cross-section of NI formation (not for all compounds), as well as low ion stability due to the autoneutralization phenomenon that is atypical of PI and therefore remained unexplained for long. Taken altogether, these circumstances complicated the design of corresponding equipment for solving basic and applied analytical problems.

They were solved upon development of resonant electron capture negative ion MS (REC NI MS).^{8–11} Beginning from the 1970s, the method was developed independently of related MS techniques^{12–15} including secondary electron capture NI MS (SEC NI MS),^{16–19} dissociative electron attachment spectroscopy (DEAS),²⁰ trochoidal electron monochromator (TEM) MS,²¹ and other MS variants based on new ionization principles (electrospray ionization (ESI), matrix-assisted laser desorption/ionization (MALDI), *etc.*). The method is characterized by unique informativity in studies of fundamental processes (reactions) of electron attachment (capture) by polyatomic molecules, dissociative decay, and autoneutralization of NI,^{11,22–24} and has a great potential for solving applied structural and analytical tasks.^{9,10,24} In this review we will analyze a large body of experimental data and generalize the most important results obtained by REC NI MS.

Electron-molecule reactions used to generate ions are shown in Fig. 1. The title method is used to detect mass-selected NI formed from isolated molecules upon single collisions with free low-energy electrons having a controlled kinetic energy E_e ($0 < E_e < 15$ eV, see Fig. 1, processes 1 and 2). Widely used electron ionization PI MS (EI PI MS) is based on electron detachment from a molecule after collision with an incident electron whose energy exceeds the threshold ionization energy (IE) of the molecule ($E_e > 7–12$ eV). The intensity of ion formation gradually increases with increasing electron energy and reaches a maximum in the range of $50 < E_e < 100$ eV. The PI mass spectra recorded at a primary electron energy of about 70 eV are well reproducible (see Fig. 1, processes 4 and 5). Contrary to this, REC NI MS is based on the phenomenon of resonant capture of a free electron by

isolated molecules resulting in the formation of temporary (transient) negative molecular ions (TNI, M^- , or compound states, or resonances).

Unlike EI, REC mainly occurs at $E_e < IE$ (see Fig. 1, processes 1 and 2), while the REC cross-section (σ_{REC}) depends strongly on the E_e magnitude and represents a series of resonance peaks characteristic of only a given compound. This is due to the fact that REC occurs only if the electron energies E_e match the energies of particular energy levels of the molecules that are unique to each compound. Using REC NI MS, one can obtain 3D mass spectra that reflect the dependence of REC on the electron energy. In the 3D mass spectra, each mass peak (Fig. 2, *a*) unfolds into an effective yield curve (EYC) of NI (Fig. 2, *b*), which characterizes the intensity of ion formation as function of the energy of electrons being attached. Thus, the total NI mass spectrum includes the energy coordinate bearing additional information on various aspects of ion formation processes (Fig. 2, *c*). It is this feature that is unique to REC NI MS and fundamentally differs this method from other versions of MS that in most cases are based on the detection of positive ions. Therefore, in REC NI MS an ion peak is meant both a peak on the m/z scale and a resonant peak on the E_e scale. One more measurable parameter is the lifetime with respect to autoneutralization (electron autodesorption lifetime), τ_a , which is characteristic of NI only and bears information on them and (or) on the properties of molecules.^{25–27}

The method of REC NI MS allows one to solve analytical problems in situations where EI PI MS is powerless. In particular, a peak of molecular ions M^- and (or) dehydrogenated ions $[M - H]^-$ observed even in the incomplete 2D REC NI mass spectrum (see Fig. 2, *a*) makes it possible to determine³⁸ the molecular weights of compounds whose EI PI mass spectra exhibited no such peaks. The fragmentation pathways of NI are simpler and better understandable than those of PI. Small number of lines/peaks inherent in the REC NI mass spectra of most compounds by no means preclude the identification of substances; rather, it facilitates the determination of the molecular structures, allows one to reveal the fragmentation channels and the characteristic ions for entire classes of chemical compounds, and to predict the mass spectra of new compounds (see Section 3). The possibility to trace the lineage of daughter NI based on the peaks of metastable ions is as efficient mean as in the case of PI MS.^{26,35,39–50} The title method enables rather accurate measurements of the appearance energies of fragment NI (E_{ap}) (see Fig. 1) and the NI lifetimes with respect to autoneutralization and dissociative decay, which allow one to determine the energy and kinetic parameters of electron-molecule reactions,²⁶ to reveal rearrangement processes, to evaluate the electron affinity (EA) of molecules and their fragments, the energies of interatomic bond rupture, gas-phase acidity, the relative enthalpies of

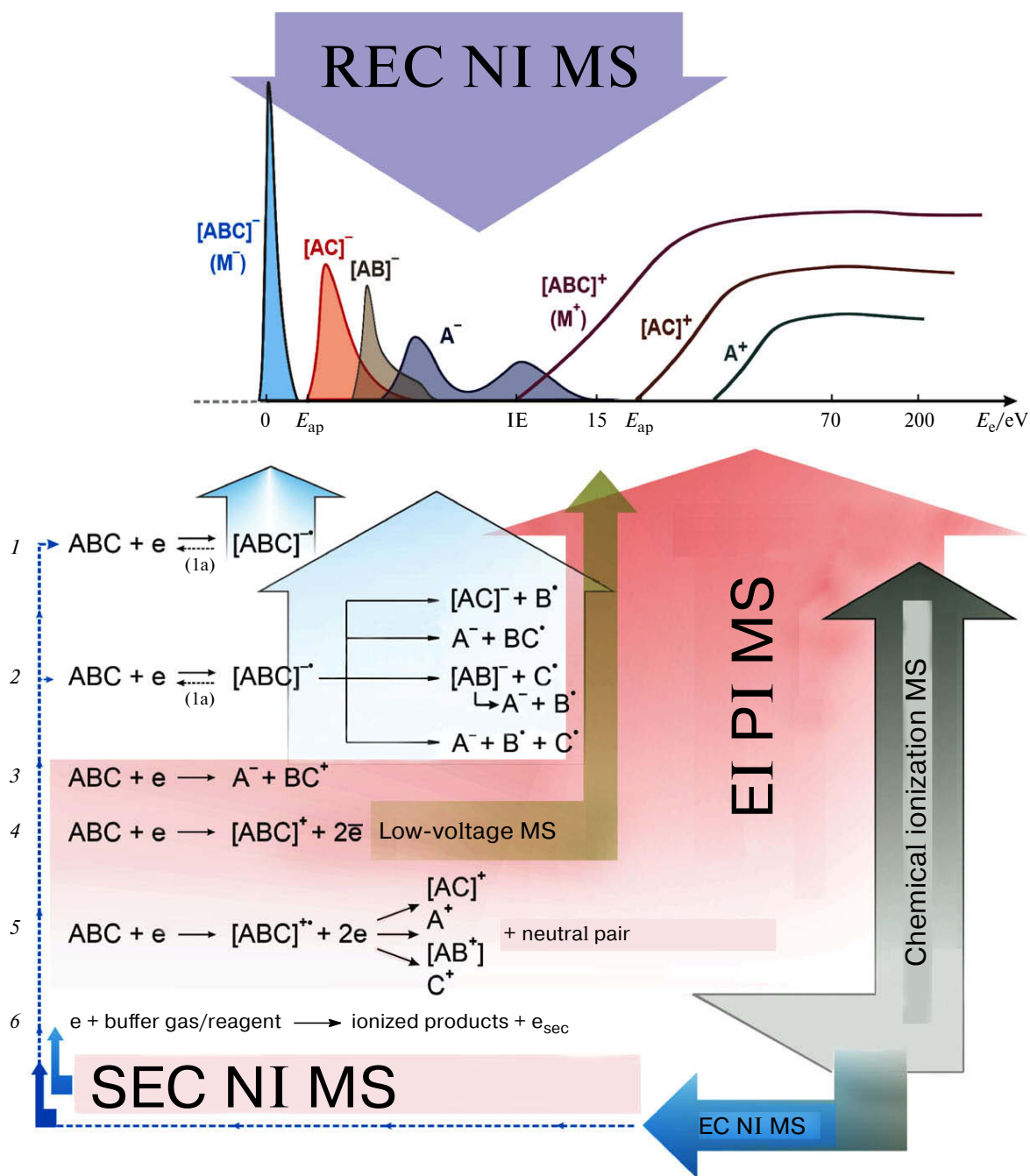


Fig. 1. Electron-molecule reactions used in mass spectrometry to generate ions and corresponding characteristic ranges of their occurrence on the electron energy scale: nondissociative (associative) resonant electron capture (1), dissociative resonant electron capture (2), polar dissociation (3), electron ionization (4), fragmentation of positive ions (5), chemical ionization, thermalization of electrons (6); IE stands for ionization energy; E_{ap} is the appearance energy; NI MS and PI MS stand for negative ion and positive ion MS, respectively; REC stands for resonant electron capture; SEC stands for secondary electron capture, EI stands for electron ionization, and EC stands for electron capture.

formation, and other thermodynamic and structural characteristics of compounds under study.^{51–63} Substance-specific discrete pattern of energy regions where NI appear, existence of strict selection rules which control the frag-

mentation of NI, and selectivity to certain channels of dissociative decay provide unique possibility to distinguish between different isomers, to reveal the arrangement of substituents and positions of multiple bonds, to sequence

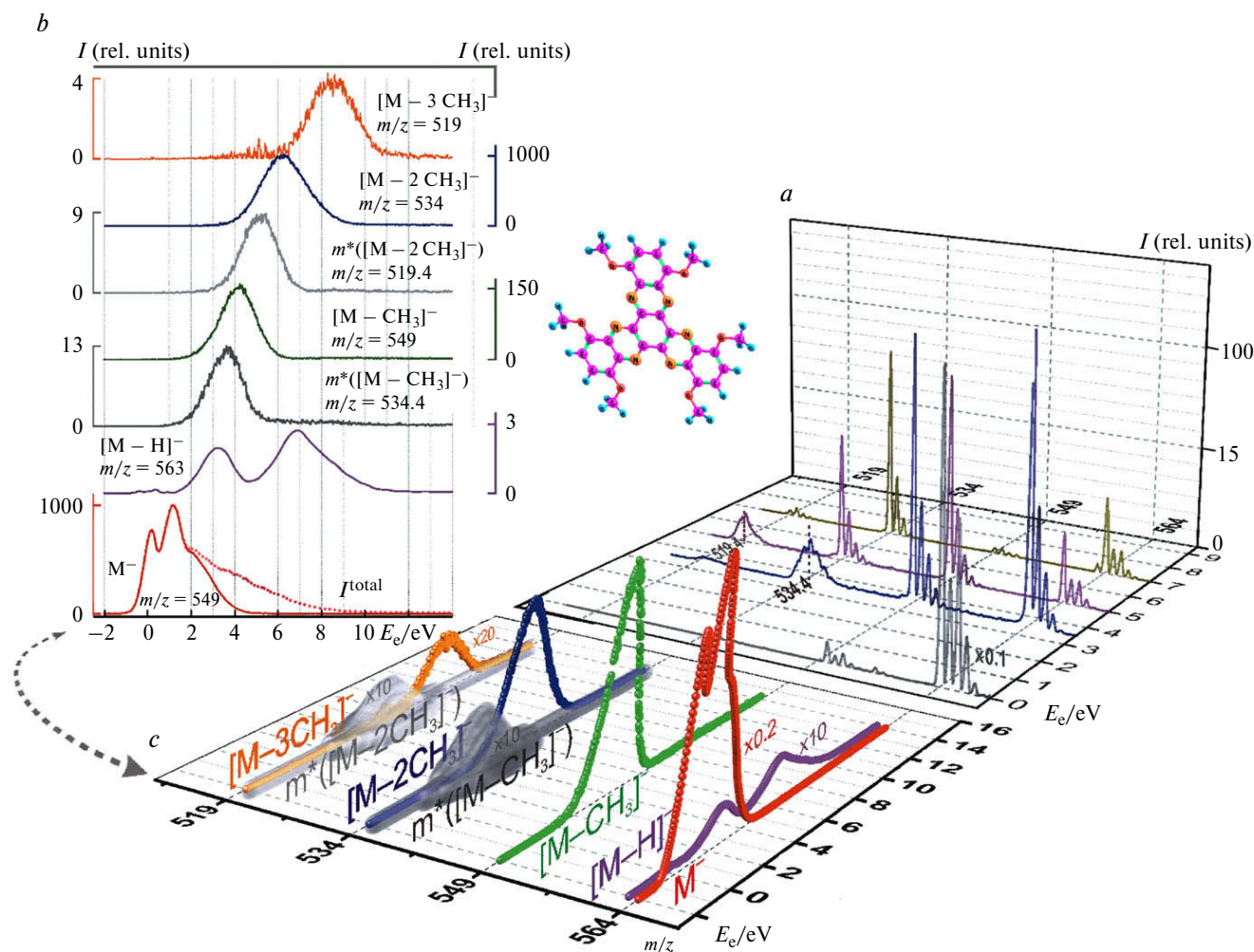


Fig. 2 Various representations of REC NI mass spectra exemplified by those of 1,4,7,10,13,16-hexamethoxy-5,6,11,12,17,18-hexaazatrinaphthylene²⁶: traditional, recorded at different fixed electron energies (*a*), negative ion effective yield curves as functions of the energy of captured electrons (*b*), and a 3D representation, secondary isotopic peaks are not shown (*c*)^{*1}; M stands for molecular ion, m^* is the "diffuse" peak characterizing fragmentation of metastable NI, and I^{total} is the total ion current.

peptides, and to analyze mixtures of chemical substances without preliminary separation (see Section 2).

For many classes of compounds the intensity of NI formation is at least comparable and even higher than that of PI formation. Molecules characterized by high (adia-

^{*1} When MS is used for analytical purposes, it is commonly accepted to represent the mass spectrum as shown in Fig. 2, *a*. The "spectroscopic" representation (see Fig. 2, *b*) is more preferable when solving fundamental problems. Three-dimensional REC NI mass spectra (see Fig. 2, *c*) are reported rarely (see, e.g., Refs 28–30). Representation of mass spectra in tabulated form with indication of the m/z (mass-to-charge) ratio, relative intensities of ion peaks, and energies corresponding to ion yield maxima is more compact but less exhibitive and self-explanatory.^{31,32} The NI mass spectra are also reported in the "icicle-like" form^{14,33} and as 2D plots where the NI intensities are displayed using various color contrast schemes.^{29,34–37}

batic) electron affinity (EA_a),^{*2} which usually have an extended π -conjugated electronic structure and/or contain aromatic fragments and strong electron-withdrawing groups, are particularly sensitive to low-energy electrons.^{21,30,57,64–69} Such compounds are not only practically valuable in various industries, but can also belong to biologically, chemically and environmentally hazardous substances. That is why they are of prime interest for detection and analysis.

The title method, REC NI MS, allows one to obtain reliable data by taking into account the ion peaks whose relative intensities are of the order of only a few hundredths of a per cent. A comparison of the peak intensities of

^{*2} They are called electrophilic,^{21,57,64,65} electronegative,^{21,30,66} electrophoric,^{67,68} electron-deficient,⁶⁹ and electron-absorbing molecules.³⁰

singly charged and corresponding doubly charged NI showed^{70–73} that in some cases the dynamic range of detection can go beyond 10^6 . Note that in the case of EI PI MS studies, especially, MS/gas chromatography (GC) ones, the attainment of wide dynamic range and efficient identification is precluded by a "palisade" of rather intense background peaks present in the mass spectra. Indeed, at $E_e = 70$ eV, all substances (including residual vapors) present in the vacuum system are ionized and undergo intense fragmentation, which leads to the appearance of undesired background noise. That is why weak ion peaks with intensities lower than 1–2% of the main peak intensity are usually ignored when substances are identified by comparing the experimental EI PI mass spectra with the mass spectra from databases.⁷⁴ However, this is not the case for the selective method, REC NI MS.

At present, full-scale REC NI MS studies using the available equipment are complicated and labor-consuming. Long time required to record the full REC NI mass spectra can also be treated as a drawback of the method. Nevertheless, the state of the art in analytical instrumentation holds out a hope of solving these problems. In particular, 3D REC NI mass spectra can be recorded within a few seconds, which is comparable with the time required for quantitative recording a GC peak.²⁹ In addition, structural and analytical studies do not require detailed investigation of fundamental properties of molecules and detection of subtle details of ion formation. Therefore, it makes the most sense to carry out express analyses and routine REC NI MS studies using only those possibilities of the method which provide highly informative, reproducible, and characteristic data sufficient for the detection and identification of chemical compounds and for quantification of the composition of the samples under study. In this case, even recording of incomplete REC NI mass spectra in the 2D form can be rather informative and structure-specific.^{60,75–78}

Mixtures of low-molecular-weight compounds are often analyzed using a combination of GC and mass spectrometry (GC/MS). The REC NI mode can be realized using basic configurations of commercially available equipment (a gas chromatograph and a mass spectrometric detector) designed for operation in the EI PI mode without significant modification (see Section 3).^{79–90} Again, no significant modification of the equipment is required. This allows one to considerably extend the built-in capacities of chromatography mass spectrometry at almost no extra cost. The most promising applications of this method (in both PI and NI modes) include detection of various ecotoxicants, chemical warfare agents (CWA), and explosives, as well as identification of biologically significant compounds.

Resonant electron capture has been intensively studied since the 1950s. The subject matter was varied with time. For instance, in the 1950–1960s the emphasis was placed

on atomic and simple small NI in connection with the determination of the isotopic composition of halogens, studies of ionospheric processes, and charge exchange for elementary particle accelerators, search for gas insulators, and progress in radiochemistry and catalytic chemistry.¹² Due to improper choice of systems to study an opinion was formed that REC NI MS is unsuitable for solving structural and analytical problems since poor ion composition, low intensity, and poor reproducibility of NI mass spectra make the method low informative. As time passed, REC NI MS has been used to study natural compounds, organic ecotoxicants, halocarbons, cluster compounds, fullerenes, compounds for plasma technologies, organic and molecular electronics, *etc.* In the XXI century the focus of research shifted to electron-induced transformations of technologically significant compounds, clusters, and biomolecules.^{91–94}

Domestic researchers contributed largely to the development of REC NI MS.^{7,95–97} The most consistent and extensive research is being carried out at the scientific school founded in the 1960s at the Bashkir Scientific Center of the USSR Academy of Sciences in Ufa.^{*3 22,23,98,99} The advances made here include the development of equipment for NI generation and detection, systematic research into ever-increasing number of molecular systems, and establishment of rules of NI formation.¹⁰⁰ Unfortunately, numerous attempts to adopt the method at other scientific institutions in the Russian Federation and to launch production of accessories to provide the possibility for commercially available mass spectrometers to operate in the REC NI mode have failed.²²

At present, REC NI MS is a method of investigation with unique capabilities and a great potential for structural and analytical studies.^{10,11} Globally, there are at most 30 research groups whose activity ever involved experiments using methods related or similar to REC NI MS including those using fundamentally new methods.¹⁰¹ The most influential scientific schools abroad are those from the USA,^{34,102} Germany,¹⁰³ France,¹⁰⁴ Austria,^{105,106} India,¹⁰⁷ and Australia.¹⁰⁸ Their interests span from physics of low-energy electron-molecule collisions to applications of NI for solving purely structural and analytical problems. Numerous publications on analytical applications of certain NI MS techniques are available (see, *e.g.*, Refs 12, 16, 38, 64, 67, 108–116); however, there are only a few studies on realization of the potential of the method in the controllable REC mode.^{21,24,30,65,117–119}

High informativity of REC NI MS is especially pronounced when studying electron-molecule collisions and physicochemical properties of chemical substances, as shown by dissertations in physics^{120–135} and chemistry^{136–141} conducted in recent decades at the Institute of

*3 From this point on, "Ufa group".

Molecule and Crystal Physics and at the Ufa Institute of Chemistry, Ufa Federal Research Centre of the Russian Academy of Sciences, respectively. However, their authors paid little attention to analytical significance and unique character of structural data that often cannot be obtained by other methods. In this review we will formulate advanced research directions to realize the applied potential of REC NI MS. It cannot be denied that at present many possibilities of the method seem to be redundant for analytical applications. Nevertheless, we consider it necessary to mention more of its advantages, regarding possible development prospects. Specific character and low prevalence of REC NI MS make it necessary to designate its place among various versions of analytical MS. To this end, we compared the title method with more traditional, conventional MS techniques. Considerable attention will be paid to recent advances made since publication of the review⁹ and monograph,¹⁰ as well as to generalization of the results obtained using this highly informative, time-proven, well-grounded and, unfortunately, undeservedly underestimated analytical method.

1. Resonant electron capture negative ion mass spectrometry: the methodology

Physical background

The challenges that one has to face when conducting research by the REC NI MS method are as follows: what ion peaks and under which conditions will dominate the NI mass spectra, at what electron energies will the peaks be observed, and what are the expected relative intensities of the peaks.

Theoretical insights into the appearance of resonances upon electron scattering by atomic and molecular targets were reported in the 1960–1970s.^{142–149} Fundamental principles of REC, as well as the properties and applications of NI have been documented in reviews and monographs^{91,93,103,105,150–166} including those published in Russian.^{9–11,23,66,143,167,168}

Resonant electron capture is meant a delay of an electron by a molecule*⁴ such that a time delay is longer than 10^{-14} s, which much exceeds the time of flight through the molecule ($\sim 10^{-17}$ s at $E_e = 10$ eV).¹⁶³ The phenomenon is observed in a wide range of electron energies from 0 to ~ 10 –15 eV, although for organometallic compounds and fullerenes the upper bound can be as high as a few tens of electron-volts,^{169–171} thus partially covering the range of ionization energies of molecules.

The kinetic energy of an incident electron to be attached to a molecule can be damped as a result of the following:

*⁴ Atomic resonances are not considered in the review.

1) vibrational excitation of the molecule (so-called vibrationally-excited, or nuclear-excited Feshbach resonance, or NEFR). This type of resonance appears in a narrow range of thermal electron energies ($E_e \sim 0$ eV) and is characteristic of molecules with positive EA_a only (Fig. 3, *a*);

2) the appearance of a potential barrier with shortening the distance between the electron and the molecule (so-called shape resonance, or SR). This usually occurs¹⁵¹ at $0 < E_e < 4$ eV (Fig. 3, *b*);

3) electronic excitation of the molecule (core-excited Feshbach resonance, or CEFR (Fig. 3, *c*), and inter-shell resonance (Fig. 3, *d*). They appear at $E_e > 2$ eV; collective plasmon excitations are also possible.¹⁷²

Specific features of and distinctions between all types of resonances have been well documented.^{10,147,153,173}

The formation energies of SR and NEFR can be directly determined by electron transmission spectroscopy^{174,175} and electron energy loss spectroscopy,^{105,176} respectively, and predicted using correlations with photoelectron spectroscopy data.^{177–183} Inter-shell resonances were revealed from explicit correlation with energies of singlet transitions in optical UV spectra¹⁷³ that can serve reliable reference points for identification of such resonances. The formation of PI is associated with detachment of an electron from the highest occupied molecular orbitals (HOMOs), while the formation of NI is associated with the appearance of an additional electron on the vacant, or virtual MOs; note that the position of the lowest unoccupied molecular orbital (LUMO) specifies the EA energy of the molecule (see Fig. 3). Rapid progress of quantum chemical methods allows one to predict the energy positions of resonance peaks with reasonable accuracy using the results of theoretical calculations of the vertical electron attachment energies (VAE) (this parameter is often treated as the vertical electron affinity energy) to vacant MOs,^{184–190} the ionization energies of occupied MOs, and the energies of transitions between the energy levels corresponding to the occupied and vacant MOs.^{191,192} The $AB^{\cdot-}$ ions formed as a result of REC (Eq. (1)) are unstable or metastable (since they have an excess energy from the attached electron and this energy cannot be released without collisions with third particles) and therefore decompose through autoneutralization (Eq. (1a)) and/or undergo fragmentation with the formation of a neutral particle and a NI (Eq. (2)). The latter process is called dissociative electron attachment (DEA)*⁵, although it involves the REC event as intermediate step. Observation of long-lived negative molecular ions in the course of process (1) is treated as a result of nondissociative (associative) electron capture:

*⁵ Not to be confused with another method having a consonant name, *viz.*, *Electron Capture Dissociation (ECD)*¹⁹³ that is used for electron-induced fragmentation of multiply charged PI by exposing them to low-energy free-electron beam.

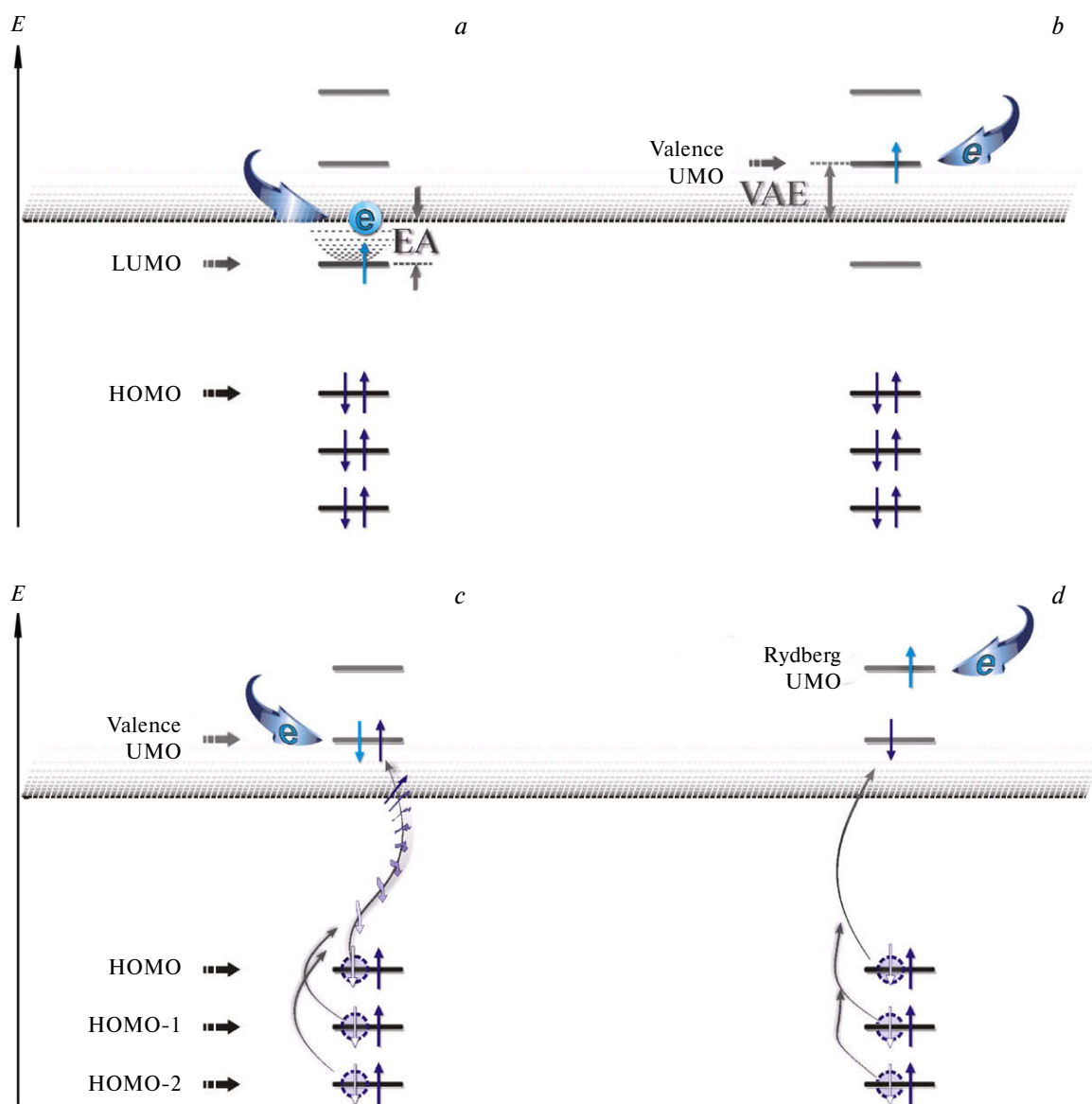
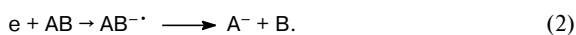


Fig. 3. Electronic configurations of negative molecular ions for different REC mechanisms: vibrationally excited (or nuclear excited) Feshbach resonance (a), shape resonance (b), a series of core-excited Feshbach resonances (c), and a series of inter-shell resonances (d); VAE stands for the vertical (electron) attachment energy and EA stands for the electron affinity.



Depending on the size of the molecule and on the energy of the resonance, fragmentation can take any time from the period of interatomic vibrations (10^{-14} s) up to the entire width of the experimental time window. Mass spectrometry is used to detect long-lived molecular ions ($AB^{\bullet-}$) with lifetimes of at least 10^{-5} s and fragment NI (A^-) formed within this time window (with rare exception, they are stable with respect to further fragmentation).

The appearance of a fragment NI, A^- , from the molecule AB (Eq. (2)) becomes possible if the energy of the captured electron is no lower than the thermochemical threshold specified by the heat of the DEA reaction (ΔH_f):

$$\begin{aligned} \Delta H_f &= \text{BDE}(A-B) - \text{EA}(A^{\bullet}) = \\ &= \Delta H_f(A^-) + \Delta H_f(B^{\bullet}) - \Delta H_f(AB), \end{aligned} \quad (3)$$

where BDE is the homolytic dissociation energy of the A–B bond, $\text{EA}(A^{\bullet})$ is the electron affinity of the charged fragment (A^{\bullet}), and ΔH_f is the enthalpy (heat) of formation of the corresponding species.

The energy threshold can shift the position of the fragment NI peak maximum in the EYCs, thus "cutting" the

low-energy wing of the resonance from which these ions are formed. A comparison of the experimentally determined appearance energies of the fragment NI measured to an accuracy of ± 0.03 eV (see Ref. 52) and the calculated ΔH_f values confirmed the tentative structure of the DEA products, which made it possible to reveal hidden rearrangements and isomerization processes.^{55,58,194,195} Taking into account the assumption that E_{ap} equals the thermochemical threshold ΔH_f , from Eq. (3) one can evaluate the unknown parameters, BDE(A–B) or EA(A \cdot). For instance, the electron affinities of [M – H] \cdot radicals formed from carbonyl compounds,⁵¹ phenols,⁵³ acridone and its derivatives, *etc.*,^{52,57} were determined using the $E_{ap}([M - H]^-)$ energies measured by REC NI MS and the O–H bond dissociation energies reported elsewhere. Moreover, experimental $E_{ap}([M - H]^-)$ values allow one to almost directly assess the relative stability of NI and the gas-phase acidity, ΔH_{acid} , (enthalpy of deprotonation) of molecules^{57,52,196} using the simple relationship:

$$\Delta H_{acid}(M) = E_{ap}([M - H]^-) + IE(H), \quad (4)$$

where $IE(H) = 13.598$ eV is the ionization energy of hydrogen atom.¹⁹⁷

The evolution of thermochemical approaches including those concerning NI was considered in monographs.^{57,198} The appearance energies of fragment ions formed from polyatomic molecules can be higher than the calculated thermochemical threshold ΔH_f due to the existence of symmetry prohibition and the so-called kinetic shift.⁷² The state of the art in computational methods of quantum chemistry allows one to calculate, with admissible accuracy, the enthalpies of formation of rather large molecules,^{199,200} which is of importance for thermochemical analysis and prediction of NI mass spectra. Recently, rapidly progressing methods using neural networks also proved themselves.^{60–63,201}

High competition between NI formation and autoneutralization (Eq. (1a)) causes a decrease in an already relatively small REC cross-section at non-thermal energies ($0 < E_e < 15$ eV). The main reason for low total intensities of the REC NI mass spectra is autoneutralization, the process which is impossible for isolated PI. The characteristic cross-sections of NI formation at non-thermal energies E_e are in the range of 10^{-16} – 10^{-19} cm². The lifetimes τ_a of negative molecular ions formed from the molecules with EA > 0 at thermal energies E_e can be very long.^{196,202} In this case, nondissociative REC dominates since the extra electron energy is often too low for bond dissociation to occur (see Eq. (3)). The larger the number of atoms in a molecule and the higher the EA of the molecule the longer the lifetime of molecular ions formed by the NEFR mechanism; therefore, the probability to detect a strong narrow peak of these ions in the mass spectrum increases.^{25,68,102,151,196,203} This interrelation underlies

a number of methods that allow one to evaluate the adiabatic electron affinity of molecules from the measured lifetime of the molecular ions M $^-$ (*e.g.*, models based on the Arrhenius equation,^{196,204–206} on the principle of detailed balance,^{102,207,208} and on the Rice–Ramsperger–Kassel–Markus statistical theory^{26,209,210}).

At thermal energies E_e , the REC cross-section (σ_{REC}) can be much larger than the ionization cross-section of a molecule (typically, about 10^{-15} cm²) and even the gas-kinetic cross-section ($\sim 10^{-14}$ cm²).¹⁵³ The maximum value of the ionization cross-section of SF₆ (elegant) molecule at $E_e \approx 105$ eV is about $6.5 \cdot 10^{-16}$ cm²,²¹¹ whereas $\sigma_{REC}(SF_6^-)$ can be as large as $4 \cdot 10^{-14}$ cm² (see Ref. 212) and even $7.617 \cdot 10^{-13}$ cm² (see ref. 213) at $E_e \sim 0$ eV. It follows that the limit of detection of this compound by REC NI MS can be two or three orders of magnitude lower than that determined by EI PI MS. Such an ultrahigh sensitivity and selectivity to compounds with high EA has attracted the attention of analytical chemists and makes NI MS indispensable tool for the detection of trace amounts of electrophilic substances. The limits of detection can reach a few attograms (1 attogram = 10^{-18} g), being record high for MS *per se*.^{67,118,214} Even if analyses in the PI and NI modes are characterized by identical sensitivity, "the latter is more preferable for analysis of complex-matrix samples, since it allows one to significantly reduce the matrix component interference, thus increasing the signal-to-noise ratio and, therefore, the sensitivity and selectivity of the analysis".²¹⁵ However, the presence of fragment NI in the mass spectra is also of importance for structural and analytical studies. Dissociative electron attachment is characteristic of all substances; therefore, REC NI MS can be used to analyze almost all compounds that can be sublimed avoiding decomposition.

The formation cross-section of NI can depend on temperature much stronger than that of PI under EI conditions; as a consequence, this influences the reproducibility of the NI mass spectra. Since the efficiency of autoneutralization increases with temperature, the intensities of the M $^-$ peaks always decrease. This feature of molecular ions can be used to determine the electron affinities of molecules.²¹⁶ Contrary to this, the yield intensity of fragment NI increases (although there are certain exceptions^{217–219}) and the maximum yield simultaneously undergoes a shift toward lower E_e .^{153,219} Usually, this is due to increasing population of higher vibrational levels of the molecule with temperature (so-called "hot-band effect"). The most pronounced temperature dependences were observed for small fragment NI formed at low electron energies ($E_e = 0$ – 2 eV), *e.g.*, halogen ions (Hal $^-$), CN $^-$, NO₂ $^-$, *etc.*^{219,220}

The characteristic distribution of fragment NI cross-sections (σ_{DEA}) among different classes of compounds is shown in Fig. 4.

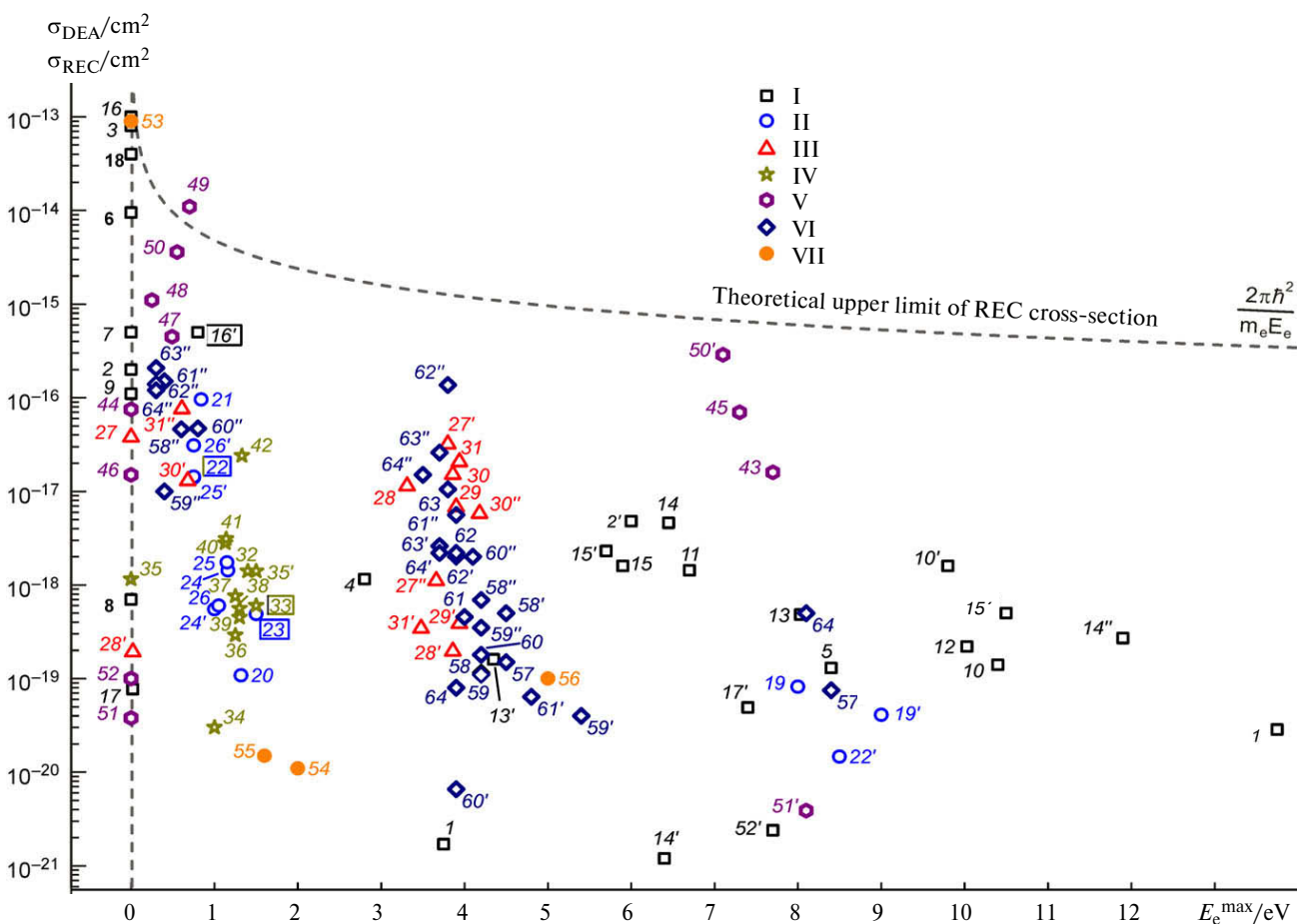


Fig. 4. Theoretically predicted region of REC cross-sections⁶⁶ and the experimentally measured REC cross-sections (σ_{REC} for M^- ions) and DEA cross-sections (σ_{DEA} for fragment ions) plotted vs. electron energy at maxima of the most intense resonances for the following groups/classes of molecules:

— small molecules (I): H^-/H_2 (1); Cl^-/Cl_2 (2); F^-/F_2 (3); C_2H^-/C_2H_2 (4); O^-/H_2CO (5); $Cl^-/CFCl_3$ (6); M^-/GeF_4 (7); Cl^- , $M^-/SiCl_4$ (8, 9); CH_2^- , H^-/CH_4 (10, 10'); O^-/O_2 (11); O^-/CO (12); O^-/CO_2 (13); H^- , OH^- , O^-/H_2O (14, 14', 14''); NH_2^- , H^-/NH_3 (15, 15'); Cl^-/CCl_4 (16); Cl^-/CH_3Cl (17); M^-/SF_6 (18) (data were taken from Refs 212, 213, 221–225 and from the publications cited in Refs 150 and 168);

— benzene and its derivatives (II): $C_6H_5^-$, C_2H^-/C_6H_6 (19, 19'); $PhS^-/PhSH$ (20); $Br^-/PhBr$ (21); Cl^- , $[M-H]^-/PhCl$ (22, 22'); $[M-H]^-/PhOH$ (23); $[M-H]^-$, $Cl^-/1,4-C_6H_4ClOH$ (24, 24'); $[M-H]^-$, $Cl^-/1,3-C_6H_4ClOH$ (25, 25'); $[M-H]^-$, $Cl^-/1,2-C_6H_4ClOH$ (26, 26');^{56,150}

— nitrobenzenes (III): M^- , NO_2^- , $[M-H]^-/PhNO_2$ (27, 27', 27''); NO_2^- , $[M-H]^-/1,2-C_6H_4NO_2NH_2$ (28, 28'); NO_2^- , $[M-H]^-/1,4-C_6H_4NO_2NH_2$ (29, 29'); NO_2^- , $[M-H]^-/1,4-C_6H_4NO_2OH$ (30, 30'); NO_2^- , $[M-H]^-$, $[M-CH_3]^-/1,4-C_6H_4NO_2OMe$ (31, 31', 31'');^{68,220,226}

— carboxylic, nucleic, and amino acids (IV): $[M-H]^-/HCOOH$ (32); $[M-H]^-/acetic\ acid$ (33); $[M-H]^-/uracil$ (34); M^- , $[M-H]^-/uridine$ (35, 35'); $[M-H]^-/proline$ (36); $[M-H]^-/valine$ (37); $[M-H]^-/alanine$ (38); $[M-H]^-/glycine$ (39); $[M-H]^-/glycine-glycine\ dipeptide$ (40); $[M-H]^-/glycine-alanine\ dipeptide$ (41); $[M-H]^-/orotic\ acid$ (42);^{45,46,227–231}

— polycyclic aromatic hydrocarbons (PAH, V): $[M-H]^-/phenanthrene$ (43); $M^-/anthracene$ (44); $[M-H]^-/triphenylene$ (45); $M^-/pyrene$ (46); $M^-/acridine$ (47); $M^-/fluoranthene$ (48); $M^-/perylene$ (49); M^- , $[M-H]^-/tetracene$ (50, 50'); M^- , $[M-H]^-/coronene$ (51, 51'); M^- , $[M-H]^-/corannulene$ (52, 52');^{106,232}

— fullerene C_{60} and its fluoro derivatives (VI): M^-/C_{60} (53); $M^{2-}/C_{60}F_{36}$ (54); $M^{2-}/C_{60}F_{48}$ (55); $[M-2CF_3]^-/C_{60}(CF_3)_{12}$ (56);^{70,73,233}

— dibenzo-*p*-dioxin (DD) and its chloro derivatives (VII): $[M-H]^-$ (57); $[M-H]^-$, $[M-Cl]^-$, Cl^- from 1-MCDD (58, 58', 58''), from 2-MCDD (59, 59', 59''), from 2,3-DCDD (60, 60', 60''), from 2,3,7-TriCDD (61, 61', 61''), from 1,3,7,8-TCDD (62, 62', 62''), from 2,3,7,8-TCDD (63, 63', 63''), from 1,2,3,4-TCDD (64, 64', 64'', respectively).¹²⁷ The numbers of compounds that are most widely used in the experiments to calibrate the scale of absolute cross-sections of NI formation are framed.*⁶

*⁶ There are also data on the cross-sections of NI formation from chloro- and bromoethylenes,²³⁴ cysteine, acetylcysteine and methionine,^{63,235} ribose and deoxyribose,⁴² etc.^{93,150,168} (not shown in Fig. 4); MCDD, DCDD, TriCDD, and TCDD is mono-, di-, tri-, and tetrachloro derivatives of DD, respectively.

There are a number of rules that allow one to understand and interpret the mass spectra. Fragmentation of ions, irrespective of their sign, obeys the principle of minimum energy and mainly proceeds *via* channels leading to thermodynamically more stable neutral and charged fragments.⁵⁷ As a consequence, one deals with preferred formation of even-electron ions that are more stable than odd-electron structures. Indeed, both PI mass spectra²³⁶ and NI mass spectra demonstrate that peaks of even-electron ions (including those of the analytically important ions $[M - H]^-$)^{10,70,71,171,237,238} are the most intense ones. However, there are certain features characteristic of the NI mass spectra only.

Basic rules of NI formation were formulated to the fullest extent possible in the review¹⁰⁰ reported in 1975, although corresponding attempts were also made by other authors (see Ref. 239). These rules allow one to exclude NI that cannot form at all or will be observed in the mass spectra under particular conditions only. Thus, fragment NI can be formed from a given resonance state only if they obey the following four rules.¹⁰⁰

The positive electron affinity rule. *Unlike the formation of positive ions where any fragment of a molecule can bear a positive charge, in the case of NI formation the additional electron is only attached to fragments with positive electron affinity.*

This rule has something in common with the Stevenson—Audier rule for PI MS, *viz.*, fragmentation of a PI proceeds in such a manner that the lower the IE of a fragment the higher the probability for this fragment to bear the positive charge.¹ However, the positive electron affinity rule is a much more strict one since it prohibits the formation of particular types of NI and thus allows one to exclude certain fragment structures. For instance, it makes no sense to expect the appearance of peaks of N^- , N_2^- , and $C_2H_5^-$ ions in the NI mass spectra since N, N_2 , and $C_2H_5^{\cdot}$ are characterized by negative EA values. As to the observed fragment ions, their formation cross-section and (or) the relative peak intensities often correlate with the EA values of corresponding (neutral) fragments, other things being equal. For instance, low intensity of CH_3^- ion peaks corresponds to low electron affinity of the species, *viz.*, $EA(CH_3^{\cdot}) = 0.08$ eV. Contrary to this, the Hal^- , NO_2^- , CNO^- , and CN^- ion peaks are the most intense ones since they correspond to high EA energies (3.613 (Cl), 3.363 (Br), 3.401 (F), 2.273 (NO_2^{\cdot}), 3.609 (OCN^{\cdot}), and 3.862 eV (CN^{\cdot})).¹⁹⁷ Often, these peaks shield much weaker peaks of more informative ions. This feature should be taken into account when analyzing the NI mass spectra of relatively small molecules where the peaks of ions corresponding to fragments with the most pronounced electron-withdrawing properties (usually, atoms or small functional groups) always predominate. Such a spectral pattern can lead mass spectroscopists working in the field of EI PI MS to a false conclusion about low informativity

of the NI mass spectrum. However, the observed spectral pattern can be used as a detection tool sensitive to a particular class of compounds, *viz.*, halogen-containing toxicants²⁴⁰ or nitrogen-containing explosives.²¹ Moreover, the characteristic REC profile manifesting itself in the EYC of NO_2^- ions can serve as a "fingerprint" of a particular nitroaromatic compound.¹¹⁹ Although experiments demonstrate intense formation of H^- ions from almost all organic (hydrogen-containing) compounds ($EA(H) = 0.754$ eV), they are analytically insignificant since the H^- peaks are composed of contributions from many residual substances that are always present in the background of the mass spectrometer.

The positive electron affinity rule is applicable to not only fragment NI, but also negative molecular ions. Indeed, the M^- peaks are observed in the REC mass spectra only for molecules with $EA_a > 0$.

Even if an expected fragment is characterized by positive EA energy, the corresponding fragment NI can be unobserved due to the following restrictions.

Symmetry selection rule for electronic states of the parent and daughter NI. *The electronic state symmetry of decay products of each resonance state always correlates with the electronic state symmetry of the parent molecular ion (resonance).*

In terms of point group theory,²⁴¹ as applied to chemistry and spectroscopy,^{242,243} an irreducible representation of a symmetry group of a NI being fragmented should include the total irreducible representation of all fragments formed from this NI. This rule was revealed in the decomposition study²⁴⁴ of dimethyl sulfide. It was found that a resonance state of Me_2S decays into symmetry-allowed S^- and CH_3^- ions rather than CH_3S^- ions, although the CH_3S^{\cdot} radical has a higher electron affinity. This rule is a particular case of a more general rule, namely, dissociation proceeds with conservation of the nodal properties of the wave functions;²⁴⁵ it is similar to the Woodward—Hoffmann symmetry rules for chemical reactions. Considering the selectivity to dissociation pathways, DEA is closer to photodissociation rather than dissociative EI.²⁴⁶ Like photoinduced dissociation of molecules (photolysis), decay of a particular spectroscopic state of a PI also obeys the symmetry selection rule. However, ionization with high-energy electrons that can *a priori* remove electrons from any occupied MO is followed by the emergence of a statistical ensemble of ions in different electronic states in the ionization chamber (IC). These states certainly include such states whose symmetry will allow PI to dissociate through one channel or another. As a consequence, the EI PI mass spectra exhibit numerous peaks of fragment ions, and this rule is of little practical importance.

In addition to the data confirming the validity of the symmetry selection rule,²⁴⁷ intense formation of Cl^- ions from π^* -type shape resonance ($E_c \approx 0.75$ eV) was reported²⁴⁸ for chlorobenzene. This would seem to be an

exception from this rule. To explain this fact, a number of hypotheses were put forward,^{249–252} and publication of Refs 252 and 253 was followed by hot discussion. It was found that a constructive decision of the problem was marked out in the initial publication,²⁴⁸ and a consensus was reached.^{56,254,255} Indeed, the formation of Cl^- ions represents no contradiction if one takes account of the following: there exists a close-lying σ^* -state, and a non-radiative transition from the primary π^* -state to this σ^* -state leads to removal of the symmetry prohibition for dissociative decay of the chlorobenzene anion. The so-called "chlorobenzene problem" refers to not only halo-substituted aromatic compounds^{39,54,55,127} and haloalkenes,²⁵⁶ but also a much wider range of compounds and, which is of importance, often accompanies the formation of analytically important $[\text{M}-\text{H}]^-$ ions.^{238,257,258}

The rule for minimum structural rearrangements upon NI dissociation. *Relatively short lifetime of negative molecular ions (10^{-14} – 10^{-15} s) with respect to autoneutralization imposes restrictions on possible bond rearrangements involving migration of atoms and atomic groups. The competition between autoneutralization and dissociation suppresses the latter processes that take relatively long time, viz., dissociation of molecular ions with the formation of negative fragment ions mainly proceeds through direct bond dissociation.*

It follows that this rule only restricts the possibility for structural rearrangements to occur rather than prohibits them. The proportion of the "rearrangement" fragments increases with the lifetime $\tau_a(\text{M}^-)$. There is a correlation such that the larger the number of atoms (especially, electron-withdrawing atoms and functional groups) in the molecule the longer the time $\tau_a(\text{M}^-)$. Indeed, the release of neutral molecules detectable from peaks of $[\text{M}-\text{H}_2]^-$, $[\text{M}-\text{H}_2\text{O}]^-$, $[\text{M}-\text{HHal}]^-$, and $[\text{M}-\text{Hal}_2]^-$ ions, $[\text{M}-\text{NO}]^-$ and $[\text{M}-\text{OH}]^-$ ions from nitro-substituted, and $[\text{M}-\text{CO}_2]^-$ ions from carbonyl compounds, etc., is often observed and can be thermochemically argued with ease; however, it can only be explained by rearrangement processes. However, the peak intensities of the rearrangement NI are much lower than those of the NI formed through simple bond dissociation. Predominance of the latter allows one to interpret the REC NI mass spectrum with ease and to identify the structure of the compound. The orientation, sequence, or mutual arrangement of structural elements can be determined by analyzing weaker characteristic peaks of the rearrangement ions.^{55,39,127,220,234}

Studies carried out in recent decades showed that explicit and hidden rearrangements in NI are no longer treated as exotic events^{37,39,42,54–56,61,133,220,231,235,257,259–262} and became a subject of thorough investigations aimed to theoretically substantiate the reasons for their nature and to evaluate various thermochemical constants.^{52,53,58,194,263}

A detailed classification of the processes in hand was proposed.^{57,58,194}

The finite time window rule for NI detection. *Owing to finite lifetime, τ , of fragment NI with respect to electron autodetachment and to the dependence of the NI lifetime on their internal (vibrational) excitation energy, only the fragment NI with $\tau > 10^{-6}$ s can be detected.*

The reason for the introduction of this rule was the assumption that not all formed NI can survive to detection. From the results of experiments^{264,265} and numerical simulation⁴⁴ it follows that the extraction time of SF_6^- ions ($m/z = 146$) from the IC is about 8.5 μs while the time of flight of ions through the mass spectrometer tube to the detector is nearly 20 μs .

If no stabilizing factors (e.g., collisions with third particles or radiative cooling) are available, negative molecular ions always have finite lifetimes τ_a . Fragment NI, especially atomic (H^- , Hal^- , O^- , etc.) and small-group ones (Cl_2^- , OH^- , CN^- , NO_2^- etc.), as well as other ions formed upon dissociation of negative molecular ions near the energy threshold, are stable. Larger fragmentation products can "inherit" the excess energy of the parent NI; as a consequence, fragment NI will also become metastable with respect to autoneutralization. For instance, $[\text{M}-\text{H}]^-$ ions from benzene, toluene, ethylbenzene, chlorobenzene, diphenylethane, and some other ions derived from nitrobenzenes²²⁰ formed in the high-energy regions from CEFR have finite τ_a .²⁶⁶ Autoneutralization is the reason for some variation of the relative intensities of peaks in the NI mass spectra recorded on instruments with different experimental time windows.¹⁸⁹

The rules presented above are concerned with three factors responsible for the ion composition of the REC NI mass spectrum, viz., the energy, symmetry, and temporal. Owing to the restrictions imposed (see above) the REC NI mass spectra include a relatively small number of peaks and the formation of ions becomes selective to particular fragmentation channels and classes of chemical compounds.

Resonant electron capture negative ion mass spectrometry: instrumentation

It is commonly accepted that no mass spectrometers capable of operating in the REC NI mode were available on the market previously; however, double-polarity instruments were produced as long ago as the 1960s.²³⁹ Studies carried out using these instruments involved not only recording NI mass spectra at specified low electron energies,⁷⁵ but also point-to-point recording of NI EYCs.^{14,267,268} However, in most cases the equipment was purposively modified for NI generation using low-energy

electrons.^{269,270} The results obtained using one of the first modified instruments were only slightly different from those of obtained using high-energy sources of NI operating at high pressure.¹² Unfortunately, no commercial mass spectrometers for full-scale operation in the REC mode were designed during nearly six decades that passed.

The equipment for REC NI MS studies should meet specific requirements. These include 1) production of high vacuum ($<10^4$ Pa) to provide conditions for single electron-molecule collisions in the IC; 2) formation of electron beams with strictly controllable energies and narrow energy distribution; and 3) the presence of a NI detector and a data acquisition system synchronized with the electron energy variator. It is also desired to measure the total ion current and to detect the neutral component of the mass-selected ion beam for ion lifetime measurements.

Researchers at the Institute of Molecule and Crystal Physics, Ufa Federal Research Centre of the Russian Academy of Sciences, carry out REC NI MS studies using modified commercial MI-1201V magnetic sector mass spectrometers for isotope analysis (Elektron Production Association, Sumy, USSR—Ukraine).^{10,269,271–273} A schematic view of the MI-1201V mass spectrometer is presented in Fig. 5, *a*. Replaceable closed-type ion sources (one being equipped with a TEM, see Ref. 274) allow one to record 3D REC NI mass spectra in a wide dynamic range and to carry out high-precision measurements. Gaseous and vaporized liquid samples are introduced using a standard inlet system, while semivolatiles solid samples are introduced *via* a tailor-made system with an inlet tube heated to 600 °C. The ion source with a heated closed-type IC provides a high vapor concentration of the analyte and control of the vapor temperature. The instrument is equipped with a system for NI lifetime measurements. To avoid signal attenuation during the NI detection, the detection system was significantly modified. Namely, the first dynode of the secondary electron multiplier, which conventionally has a high negative potential, was connected to ground, so the data acquisition system now has a high positive potential and requires insulation and specific switching/decoupling with external devices. The research mass spectrometer uses no conversion dynode (CD) since this device does not allow one to detect the current of the neutral component of the ion beam and to measure the NI lifetimes. In addition, the principle of operation of the CD is such that the response to oppositely charged ions is unpredictable, which can significantly distort the results of measurements of the absolute cross-sections of NI formation.

Generally, recording mass spectra using static (magnetic) mass spectrometers is time-consuming. Therefore, these instruments are gradually replaced by dynamic (quadrupole (Fig. 5, *b, c*), time-of-flight (TOF)) and ion-

trap instruments that use new ionization techniques (for their evolution, see Refs 22 and 276–283)^{*7}.

Although magnetic sector mass spectrometers are worn and outdated and have significant drawbacks (long time for recording mass spectra, bulkiness, limited mass range from 1 to 2000 Da (typically)), they offer the possibility to detect peaks of metastable ions and to utilize the standard EI mode to the fullest extent, which is of great importance for structural and analytical studies. When necessary, one can rapidly switch to recording conventional EI PI mass spectra and ionization efficiency curves (provided that the possibility of scanning the electron energy is available), while the instrument equipped with TEM allows one to carry out high-precision studies of PI formation including measurements of the ionization energies of molecules and the E_{ap} energies of fragment PI.^{43,169,285} Thus, joint use of PI and NI MS considerably increases the informativity of experiments and significantly extends the range of tasks to be solved.

The design of the IC and the ion source is optimized to operate with difficult-to-control low-energy electrons and to form intense NI beams in order to improve the reliability of detection. When studying physical processes, the mass number (m/z) dimension is only necessary to detect and/or to choose ions formed from an analyte or from a reference compound. Ion signals are recorded at a fixed m/z value as the ion EYCs synchronously with scanning the electron energy E_e . Therefore, particular attention is paid to the formation of an electron beam with strictly controllable parameters, to the linearity of the E_e scale, and to maintenance of constant electron energy resolution in the entire E_e range of 0–15 eV. In particular, to prevent the interference of secondary electrons with uncontrollable energies, the diaphragms on the way of the electron beam and the inner walls of the IC are thoroughly blackened with soot. Every experiment involves a zero E_e calibration procedure and a linearity test of the E_e scale using two NI peaks with well-known energies at peak maxima and/or with the appearance energies from the reference samples (Fig. 6) that are introduced along with the analyte sample or separately (SF_6 , $C_6H_5NO_2$, NH_3 , C_6H_6 , CH_3COOH , CCl_4 , CO , CO_2 , *etc.*).^{51,104,168,213,286–288}

Setting up the ion source involves choosing the electrode potentials of the electron and ion duct in such a manner that the achieved optimum resolution and linearity of the E_e scale be not accompanied by the large "tilt" of the ion current intensity between the NI formed in the most difficult-to-control energy range 0–1 eV and the NI formed in the remaining range of 1–15 eV.^{56,289}

*7 At present, the magnetic sector mass spectrometer remains the gold standard for dioxin analysis and is the only type of mass spectrometric detector allowed in many countries for regulatory analytical methods when carrying out forensic analysis.²⁸⁴

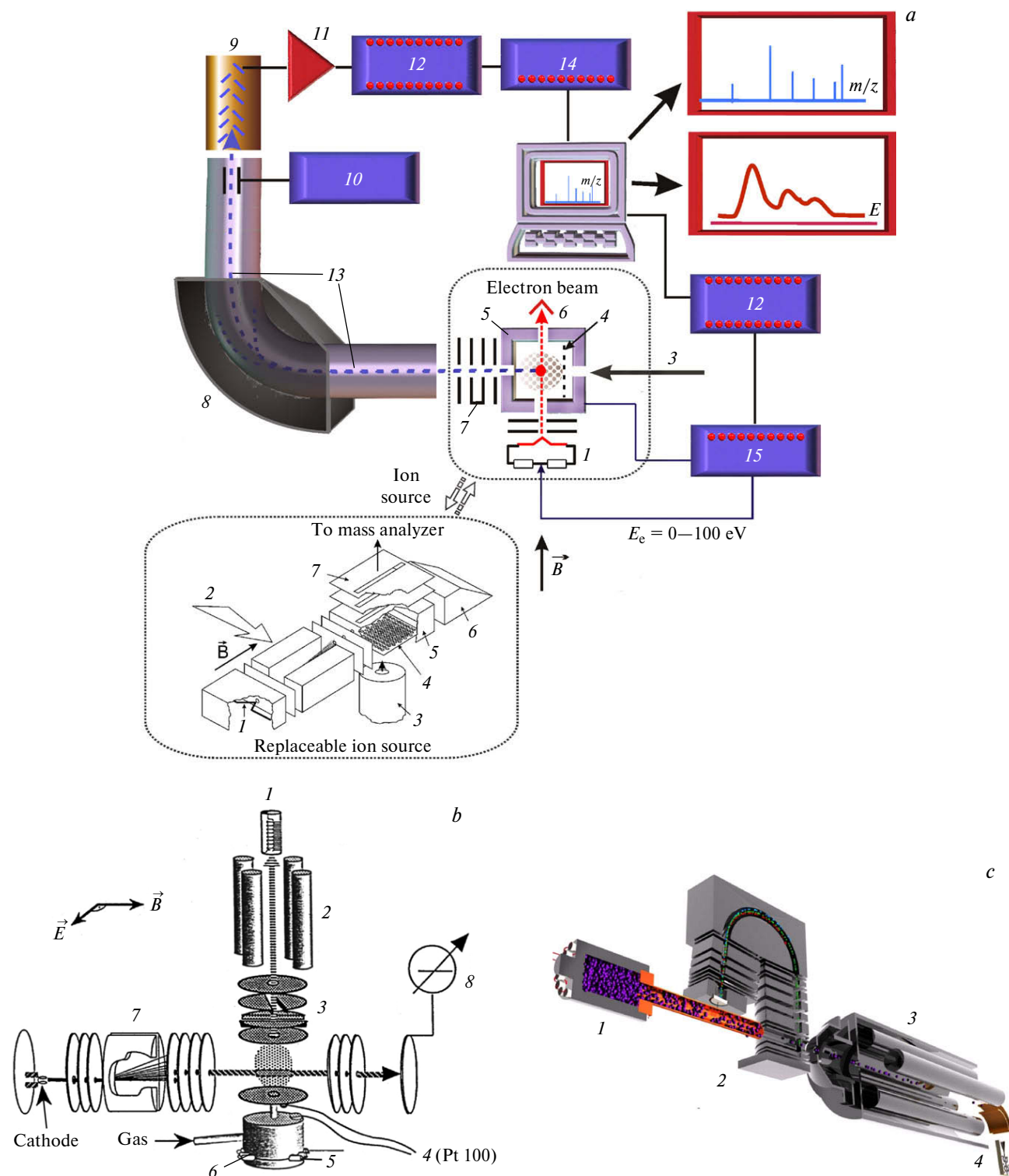


Fig. 5. Schematic view of mass spectrometers for REC studies: MI-1201V mass spectrometer (a); dissociative electron capture spectrometers with a quadrupole mass analyzer and different monochromators, viz., trochoidal electron monochromator (TEM) (b)²⁷⁵ and hemispherical electron monochromator (c).⁷⁶ Figure 5, a: cathode (1), TEM (2), inlet system tube (3), repeller (4), ionization chamber (5), electron collector (6) ion-beam forming optics (7); mass analyzer magnet (8), secondary electron multiplier (SEM) (9), deflection plates (10), d.c. amplifier (DCA) (11), optocoupler (12), field-free regions (FFR-1 and FFR-2) (13), analog-to-digital converter (14), and digital-to-analog converter (15). Figure 5, b: SEM (1), quadrupole mass analyzer (2), ion lenses (3), thermistor (4), heater (5), oven (6), trochoidal electron monochromator (7), and nanoampermeter (8). Figure 5, c: oven (1), hemispherical electron monochromator (2), quadrupole mass analyzer (3), and ion detector (4). Figure 5, b is courtesy of AIP Publishing.

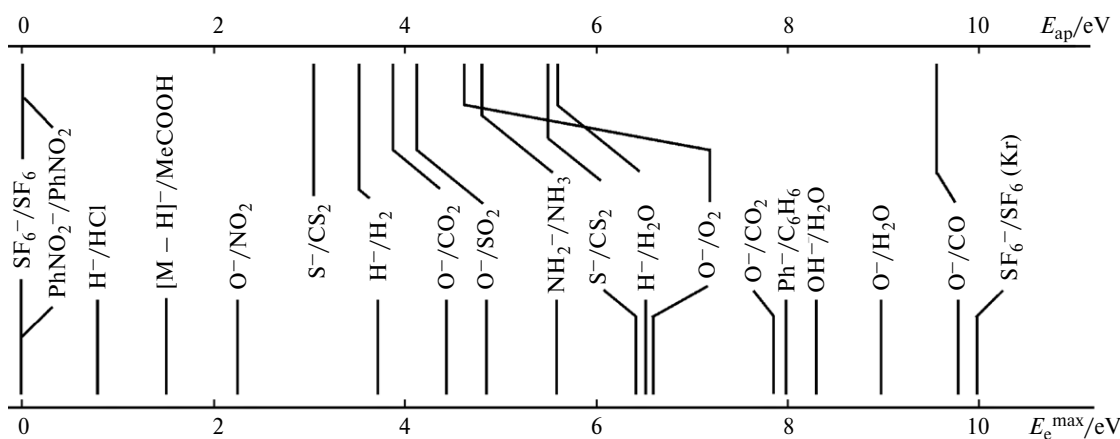


Fig. 6. The peak maximum (E_c^{\max}) and appearance energy (E_{ap}) calibrants for electron energy scale calibration (data were taken from Refs 11, 51, 104, 168, 213, 286–288).^{*8}

Otherwise, one deals with artifacts^{57,194} leading to inter-instrument irreproducibility of data and to contradictory results reported by different research groups (*cf.* the data from Refs 249 and 21 on the one hand and those from Refs 56, 220, and 290–293 on the other hand).

An increase in the electron energy resolution is achieved with the use of electron monochromator and allows one to separate close-lying resonance peaks,⁵⁶ to carry out highly accurate measurements of the energies of the peak maxima (E_c^{\max}) and the appearance energies of fragment ions,^{51,52,55} to reveal a vibrational fine structure in the cross-section of dissociative electron attachment,^{257,258,288} and to correctly reproduce the true intensity and shape of the narrowest resonance peaks^{230,294} including those appeared in the range of thermal energies. The electron monochromator plays an important role in the studies of the NI structure and the mechanisms of dissociative processes; however, it should not be overestimated when solving routine analytical tasks. The reasons are as follows. First, the ion signal becomes unreasonably weak due to low electron current; this can lead to loss of analytically significant information. Second, this is a sophisticated and somewhat "stubborn" device that should be correctly adjusted, maintained, and operated by skilled personnel (*cf.*, for instance, suppression of the intensity of a narrow $\text{C}_{60}^-/\text{C}_{60}$ peak at thermal energies E_e reported in Refs 295 and 296 and the data from Refs 294 and 297). Third, the characteristics of the monochromator can unpredictably vary due to minor contamination of the electrode surface with dielectric films that are unavoidably formed during

the operation with large amounts of substances introduced into the instrument; this influences the reproducibility of experimental data.

Resonant electron capture negative ion mass spectrometry and related experimental techniques

From the standpoint of fundamental principles and technological capabilities, DEAS (see Refs 103 and 105) is the closest analogue to REC NI MS. Recently, the abbreviation "DEAS" has been used by certain researchers from the Ufa group (see, *e.g.*, Refs 189, 298, 299), although it makes no mention of nondissociative electron capture which can also be studied by this technique. We believe that the name of the title method (resonant electron capture negative ion mass spectrometry, REC NI MS) with the focus on the mass spectrometric component and including the term "resonant" allows one to avoid confusion (see, *e.g.*, Refs 58, 252, 253, 300) with other REC-based versions of mass spectrometric analysis that operate with electrons having uncontrollable energies. These include^{301,302} electron capture ionization MS (ECI MS), electron capture negative ionization MS (ECNI MS),¹⁸ and secondary electron capture negative ion MS (SECNI MS)¹⁷ (see Fig. 1).

The equipment for DEAS studies^{103,105,303–306} is rarely used for analytical purposes *per se*. DEAS studies are carried out using laboratory-made experimental setups equipped with a quadrupole or TOF mass analyzer and an open-type crossed-beam ion source (see Fig. 5, *b* and *c*). The variety and worldwide locations of the DEAS instruments have been described in detail in the review.⁹³ The first TEM-based instrument with the possibility of mass selection of NI was constructed in 1979.²⁰ A schematic view of an instrument with a hemispherical electron monochromator is shown in Fig. 5, *c*.⁷⁶ The actual design

^{*8} Zero drift on the appearance energy (E_{ap}) scale toward negative electron energies E_e is a peculiar feature of REC NI MS. The appearance of NI in the negative region of the kinetic energy scale used to display the NI EYCs results from the finite electron energy resolution, where the fastest electrons from the high-energy wing of the distribution penetrate into the ionization chamber regardless of the negative retarding potential applied.

does not provide for the presence of an IC and is used in studies of NI formation under conditions closest to single electron-molecule collisions. This leads to low concentration of NI formed immediately in the molecular beam and, correspondingly, to a relatively weak ion signal. Nevertheless, experimental data thus obtained are only slightly different from those obtained at Ufa group, being mainly due to different ion times-of-flight, which influence the peak intensities of temporary ions.¹⁸⁹

A particular direction of NI MS for analytical applications emerged almost independently of the secondary electron techniques. In the case of ECNI MS the introduction of buffer gas into the mass spectrometer requires an additional chemical ionization system and high-performance vacuum pumping equipment. In the late 1990s it was proposed³⁰ to form a monochromatic beam of thermal electrons with controlled energy in high vacuum instead of using uncontrollable and poorly reproducible thermalization*⁹ of secondary electrons in a dense buffer gas. The idea was to identify compounds not only by the presence and relative intensities of a certain group of peaks in the NI mass spectrum, but also by the characteristic pattern of resonance features in the EYCs for each type of NI (energy profile). Monochromatization of the electron beam gave rise to the emergence of a new technique of analytical MS, *viz.*, electron monochromator MS. The main goal was to pass from poorly reproducible secondary electron ionization techniques to improved version of REC NI MS as more reliable method.

Many authors proposed tentative names and abbreviations, from *Trochoidal Electron Monochromator MS* (EM-MS or TEM-MS),^{65,117} *Tunable-Energy Electron Monochromator MS* (TEEM GC/MS), and *Low Incident Energy Electron Impact Ionization MS* (LEEIMS)³⁰⁷ to *Discrete Energy Electron Capture NI MS*.³⁰ Corresponding magnetic sector mass spectrometers were designed and implemented in cooperation with JEOL USA, Inc. (USA), the manufacturer of analytical equipment.¹¹⁹ Further progress in this direction was made by implementation the key features of REC NI MS using fast TOF technique.²⁹ High acquisition rate (within a few seconds) of 3D REC NI mass spectra is achieved by streaming NI EYCs synchronously with scanning the ionizing electron energy, which made it possible to design a GC/REC TOF mass spectrometer.^{34,234}

Recording analytically significant REC NI mass spectra does not require high electron energy selectivity; moreover, this seems to be contraindicated. Indeed, most analytical problems can be solved using 2D REC mass spectra recorded at a fixed electron energy E_e corresponding to the most intense resonance peak,^{60,65,75–78,86,118,308–311} which significantly reduces the analysis time. However,

*⁹ Deceleration of electrons to thermal energies characteristic of EC NI MS.

recording a single NI mass spectrum at a fixed energy E_e can be accompanied by missing analytically significant NI peaks that are not formed from the resonance at a given energy due to thermochemical or symmetry prohibition but can appear in neighboring resonances. Unfortunately, there are no ion sources that would simultaneously emit electrons in the entire REC energy range from 0 to 15 eV. To extract a maximum amount of information from the NI mass spectra, they were repeatedly recorded at different energies E_e that were varied with a certain increment and then the full mass spectrum was composed.^{76,312} Researchers from different groups^{21,123,127,272,313,314} independently proposed and implemented the acquisition of mass spectra by accumulation (summation) of the ion signal synchronously with electron energy ramping in a specified energy range on going along the m/z scale. Recently, a similar method for recording the cumulative (integrated) REC NI mass spectra was implemented on a commercially available GC/MS instrument comprising a gas chromatograph and a mass spectrometric detector operating in the NI mode (JSC SDO Chromatec, Yoshkar-Ola, Russia).^{85,315,316}

2. Resonant electron capture negative ion mass spectrometry: certain applications and advantages

Determination of molecular weight

A peak of a molecular ion of any sign in the corresponding mass spectrum is the most important identification feature of a chemical compound and allows one to determine its molecular weight. Having proved the correspondence between a peak with the maximum m/z value and the molecular ion,^{*10} one can identify a compound under study with ease.

However, an analysis³¹⁷ of mass spectral databases showed that peaks of molecular ions M^{+} with analytically significant intensities (at least 5% of the intensity of the main peak) are recorded only for 37% of known low-molecular-weight compounds. The main reason why positive molecular ions cannot be detected neither at $E_e = 70$ eV nor at lower energies of ionizing electrons consists in rapid fragmentation.⁵⁸

Experience showed that molecular ion peaks not observed in the PI mass spectra can often be observed in the NI mass spectra. Thus, the drawback of EI PI MS (low intensity of M^{+} peaks) can be compensated using NI MS.

*¹⁰ In the case of EI PI MS, this can be proved by recording the mass spectrum at $E_e = 10–20$ eV, which is somewhat higher than the threshold ionization energy, but *a priori* lower than the formation energy of fragment PI (so-called "low-voltage" MS,⁵⁷ see Fig. 1).

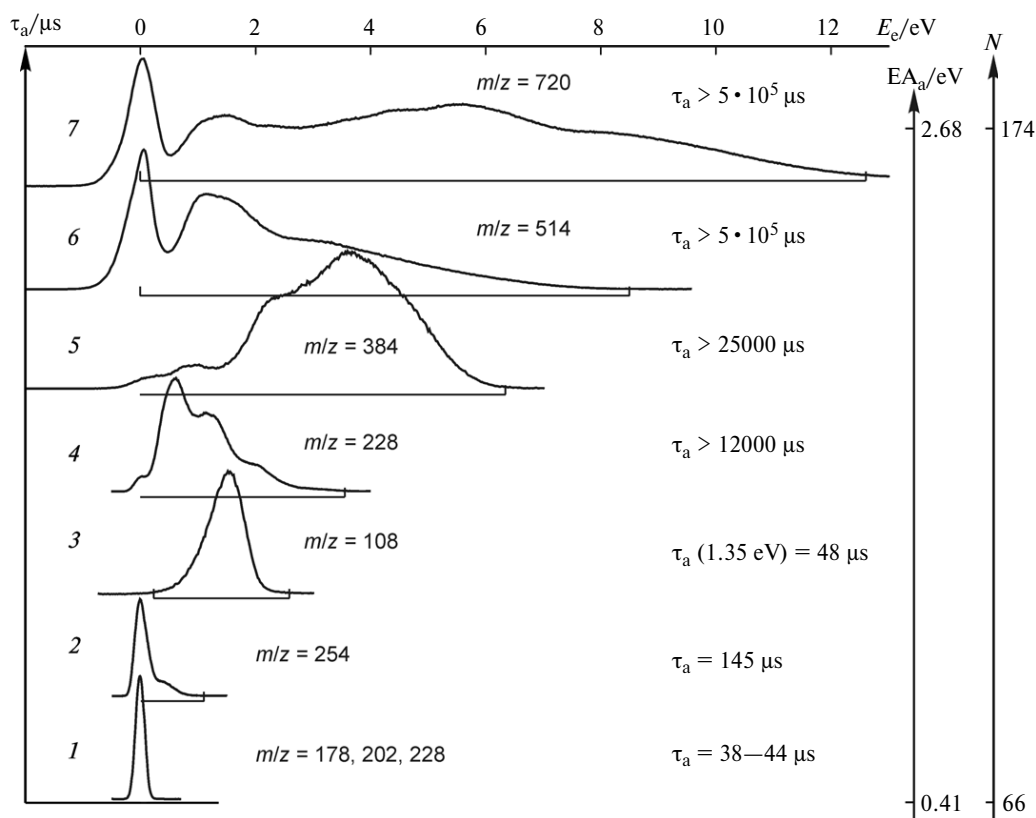


Fig. 7. Correlations between the lifetime (τ_a) and effective yield energy range of long-lived negative molecular ions on the one hand and the adiabatic electron affinity (EA_a) and the number of vibrational degrees of freedom (N) on the other hand exemplified by the data for poly- and macrocyclic compounds and *p*-benzoquinone taken from Refs 25, 26, 165, 172, 196, 197, 292, 322, 323 (see Table 1): chrysene, tetraphene, pyrene (1); 9-phenylanthracene (2); *p*-benzoquinone (3); tetracene (4); hexaazatrinaphthylene (5); phthalocyanine (6); and fullerene (7).

The advantage of REC NI MS is that peaks of molecular and fragment ions are almost always observed at different electron energies.

Compounds with positive adiabatic EA (EA_a) form long-lived negative molecular ions M^- by capturing thermal electrons ($E_e \sim 0$ eV). The appearance of the M^- peaks

in the mass spectra of compounds with high EA_a can be precluded by intense autoneutralization which intensifies with temperature. For instance, the mass spectra recorded with a magnetic sector mass spectrometer exhibit the M^- peak of chrysene ($EA_a = 0.41$ eV) (Fig. 7, Table 1), whereas the M^- peak of its less electrophilic isomer, triphenylene

Table 1. Adiabatic electron affinity (EA_a) and the number of vibrational degrees of freedom (N) for poly- and macrocyclic compounds and *p*-benzoquinone (see Fig. 7)*

Spectrum	Compound	m/z	N	EA_a /eV	Reference
1	Chrysene	228	84	0.41	165
1	Tetraphene	228	84	0.69	165
1	Pyrene	202	72	0.58	165
1	Anthracene	178	66	0.68	165
2	9-Phenylanthracene	254	96	0.80	165
3	<i>p</i> -Benzoquinone	108	30	1.85	197
4	Tetracene	228	84	1.06	165
5	Hexaazatrinaphthylene	384	120	2.15	26
6	Phthalocyanine	514	198	2.07	196
7	Fullerene C ₆₀	720	174	2.68	197

* $N = 3n - 6$, where n is the number of atoms in the molecule.

($EA_a = 0.29$ eV), is not observed.²⁵ In principle, if the EA_a value of the analyte molecule is known or can be evaluated using methods of quantum chemistry, the appearance of the M^- peak in the mass spectrum of the analyte recorded on a given mass spectrometer can be predicted using theoretical models.

The M^- peaks can appear not only at thermal electron energies, but also at non-thermal ones. Certain quinones³¹⁸ and perfluorotetrahydrofuran³¹⁹ seem to be the only group of compounds with high positive EA_a that form no long-lived negative molecular ions at $E_e \sim 0$. Peaks of M^- ions are observed in the mass spectra of these compounds only at $0.5 < E_e < 3$ eV. The formation of abnormally long-lived negative molecular ions at non-thermal energies E_e was a subject of thorough multi-year research taking quinones as examples^{298,300,320–328} and discussions of the mechanisms of long-time retention of the additional electron by the *a priori* short-lived SR and CEF. ^{196,329–332} The phenomenon was also observed for other molecular systems.^{25,179,208,271,292,319,333–335}

The electrophilicity of a molecule is characterized by the EA_a value which increases with increasing the number of electron-withdrawing groups (Hal, NO_2 , CN, CF_3 , etc.) and the number of atoms in molecules. As a consequence, the formation cross-section of NI, the lifetime $\tau_a(M^-)$ and, hence, the peak intensities of M^- ions in the mass spectra increase. One has to admit that REC NI MS is eminently suited for studying large molecules; the main requirement is that the compounds to be analyzed be sufficiently volatile. Contrary to this, an analysis of EI PI mass spectral libraries shows that the larger the molecule and the more complex its structure the lower the probability to observe a peak of positive molecular ion in the mass spectrum. Extension of the electron energy range where long-lived negative molecular ions appear is due to an increase in EA_a and in the number of atoms in the molecule (number, N , of vibrational degrees of freedom) (see Fig. 7 and Table 1).^{25,26,196} Note that no negative molecular ions were detected for naphthalene ($EA_a = 0.15$ eV,¹⁶⁵ $N = 48$), phenanthrene ($EA_a = 0.31$ eV,¹⁶⁵ $N = 66$), and triphenylene ($EA_a = 0.29$ eV,¹⁶⁵ $N = 84$).^{25,292} Compounds characterized by the most extended ranges of electron energies E_e corresponding to formation of long-lived negative molecular ions include macrocyclic systems (phthalocyanine and porphyrin)¹⁹⁶ and polycyclic aza-aromatic compounds²⁶ for which the M^- ions are detected up to $E_e = 5–8$ eV (see Fig. 7), as well as fullerenes ($EA_a > 2.6$ eV). Namely, the energy range of formation of long-lived NI M^- partially covers that of ionization energies for C_{60} and C_{70} ($E_e \approx 0$ eV to 12–14 eV)^{172,294,336} and extends to nearly 20 eV for higher fullerenes C_n ($n = 76, 78, 80, 84, 90$) with increasing the number of atoms.^{337–339}

No fragment NI are usually formed at low electron energies E_e since the energy is too low for dissociative

decay to occur. Exceptions include halogen molecules and molecules of biologically active heteroorganic compounds. Intense fragmentation of certain organohalogen and cyano compounds with the formation of Hal^- and CN^- ions occurs even upon attaching a nearly thermal electron since DEA is an exothermic process (see Eq. (3), $\Delta H_r < 0$).^{39,91,93,168,218,219,252,253,299,340–342} Biologically significant heteroorganic compounds,⁹² such as hormones,^{185,186,259} amino acids and nucleobases,^{61,63,231} sugars and their derivatives (nucleosides),^{42,60,62,261,343} as well as drugs^{50,82,327,344–347} rapidly decompose in reactions with thermal electrons. In these cases, dissociative decay processes accompanied by energetically favorable isomerization or various rearrangements are possible.⁵⁷ Therefore, if a NI mass spectrum recorded at a thermal energy E_e exhibits the only peak that differs in m/z from peaks of the known electron-withdrawing atoms or groups, it highly likely corresponds to molecular ions M^- ; this is a sufficiently reliable procedure for the determination of the molecular weight of the substance under study. Note that strong peaks of negative "molecular" ions are also recorded for free radicals, which enables mass spectrometric identification of such systems with ultrahigh sensitivity.³⁴⁸

If the mass spectrum exhibits no M^- peak, the molecular mass of the compound under study can be determined from the peak of "quasi-molecular" fragment NI (dehydrogenated molecular ions, deprotonated molecules) $[M - H]^-$.^{38,302} The exceptions are only haloalkanes and certain organohalogen compounds that often have single (Hal^-) peak mass spectra. It is the $[M - H]^-$ peaks that the most characteristic ones in the NI mass spectra of the vast majority of other hydrogen-containing (*i.e.*, organic, organometallic, inorganic, cluster) compounds.⁹ Since these mass spectral peaks are the strongest ones, they are even more significant for analytical applications than the M^- peaks that are detected not for all compounds. Usually, $[M - H]^-$ ions are most efficiently formed from organic compounds at $E_e < 2$ eV through abstraction of a (carboxyl, hydroxyl, amino) hydrogen atom substituting the heteroatom. Therefore, the odd- m/z peak with the highest m/z value observed in the NI mass spectrum will most likely correspond to $[M - H]^-$ ions (except the case for compounds with odd numbers of nitrogen atoms).

Like other fragment ions, the $[M - H]^-$ ions can be observed at different energies E_e or in several resonances. The $[M - H]^-$ peaks of compounds belonging to a particular class or containing identical structural fragments can appear in the same energy range. For instance, the E_e energy range of 1–2 eV is characteristic of the appearance of the most intense $[M - H]^-$ peaks of compounds containing OH and NH_2 groups (*cf.* $E_e \sim 4$ eV for nitrobenzenes and $E_e \approx 7.5$ eV for polyaromatic hydrocarbons²⁶¹ (see Fig. 4)).

Discrimination between isomers

The presence of peaks of negative molecular ions in the REC NI mass spectra depends on the E_{A_a} values that can vary over a wide range even for structurally similar compounds.²⁵ In some cases, rather intense peaks of negative molecular ions were observed for certain structural isomers while no peaks were observed for other isomers. Examples are provided by *o*-carborane vs. *m*- and *p*-carboranes,³⁴⁹ anthracene vs. phenanthrene,^{232,293} and other four-membered PAH vs. triphenylene²⁵ (see Fig. 7). At the same time, attempts to discriminate between isomers using almost identical PI mass spectra failed. It was reported that isomers can be discriminated using the M^- peak at non-thermal energies E_c for hydroxynaphthoquinones²⁹⁸ and coordination macrocyclic metal complexes,²⁸ however, these are only particular examples of successful discrimination between isomers from the presence (or absence) of M^- peaks in the REC NI mass spectra. In this Section we will dwell on the more widely observed situation, *viz.*, differences between the REC NI mass spectra with respect to fragment NI. According to the rule for minimum structural rearrangements, fragmentation of NI under the REC conditions mainly occurs through simple bond dissociation; however, rearrangements are often of more importance for discrimination between isomers.

The cross-sections of formation of the same ions from structurally similar compounds measured at the maximum of a resonance can differ by several orders of magnitude (see Fig. 4). Moreover, mutual arrangement of substituents can influence the electronic structure of the parent anion in such a manner that the formation of certain fragment ions will be completely suppressed but channels for the formation of other fragment ions will open. For instance, the peak of $[M - CH_3]^-$ ions ($m/z = 67$) from 1-methylimidazole observed in the REC NI mass spectra of methylimidazole isomers¹⁸⁸ at $E_c = 1.8$ eV predominates, whereas the REC NI mass spectrum of isomeric 2-methylimidazole exhibits no corresponding ion peak. In turn, the main peak in the NI mass spectrum of 2-methylimidazole is that of $[M - H]^-$ ions ($m/z = 81$), which is not observed in the NI mass spectrum of 1-methylimidazole. One more example is provided by two natural sugars, glucose and fructose. The EI mass spectra of these isomers are almost indistinguishable from each other.³⁵⁰ Under the REC conditions almost all ions from these compounds are formed at thermal energies E_c owing to deep fragmentation of negative molecular ions accompanied by energetically favorable rearrangements. No peaks of negative molecular ions were found in the REC NI mass spectra.⁶⁰ The REC NI mass spectra recorded at $E_c \sim 0.1$ eV are presented in Fig. 8. Here one deals with similarity between the ion compositions of the mass spectra of the sugars on the one hand and with significant intensity differences between

the peaks with m/z 71 and 101 on the other hand; the latter feature allows one to discriminate between the two isomers with certainty.

The sensitivity of REC NI MS to position of the double bond in the molecule is even more impressive.^{351–353} For instance, the NI mass spectra of cyclopentenyl-substituted anilines demonstrate the NI peaks corresponding to elimination of the cyclopentenyl moiety only in the case of allylic double bond, thus making it possible to distinguish between these molecules and isomers with the vinyl double bond.³⁵²

Such a high fragmentation selectivity of DEA processes compares favorably with dissociative EI. In the latter case one deals with simultaneous formation of an ensemble of positive molecular ions in different electronic states; therefore the importance of each dissociative channel is negated mainly due to possible isomerization that can proceed with ease owing to infinitely long PI lifetime.

The advantages of REC NI MS should be used to the greatest extent for qualitative and quantitative analysis of isomers. Explicit differences between the NI mass spectra recorded under DEA conditions were reported for various isomeric fluorobenzenes of different degree of fluorination,³⁵⁴ pesticides,²¹ haloalkanes,³⁵⁵ bromine-substituted phenalenones,³⁵⁶ chlorophenols,⁵⁵ hydroxybenzoic acid,¹⁸⁵ polyenes, alkylbenzenes, xylenes, *etc.*^{9,10} They are clearly seen even in the NI mass spectra recorded in incomplete 2D form. For instance, positional (structural) isomerism was observed in the mass spectra of nitrotoluene isomers,^{76,89} while identification of stereoisomers was carried out taking the lewisite isomers as examples.⁸² It is fair to say that optical isomers of L- and D-tryptophan appeared to be indistinguishable by REC NI MS.³⁵⁷

Now we will consider in more detail a representative example for analytical MS, namely, differences between the mass spectra of isomers of polychlorinated dibenzo-*p*-dioxins (PCDDs), stable environmental contaminants that are most toxic to humans. Owing to low maximum permissible concentrations, they should be analyzed using highly sensitive methods having low limits of detection. In mass spectrometric analysis, this is traditionally achieved by operating in the selected ion monitoring (SIM) mode. Among numerous congeners, the most toxic are PCDDs containing Cl atoms in β -position relative to oxygen atoms. A great threat to human health comes from 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD), the reference compound to which the toxicities of other dioxins and dioxin-like chemicals are compared. In this connection, one should have an analytical method for identification of particular isomers. Chromatomass spectrometry enables preliminary separation of components of mixtures of PCDD congeners using tailor-made chromatographic columns. When the chromatographic retention times are calibrated using the reference mixtures of dioxins, the

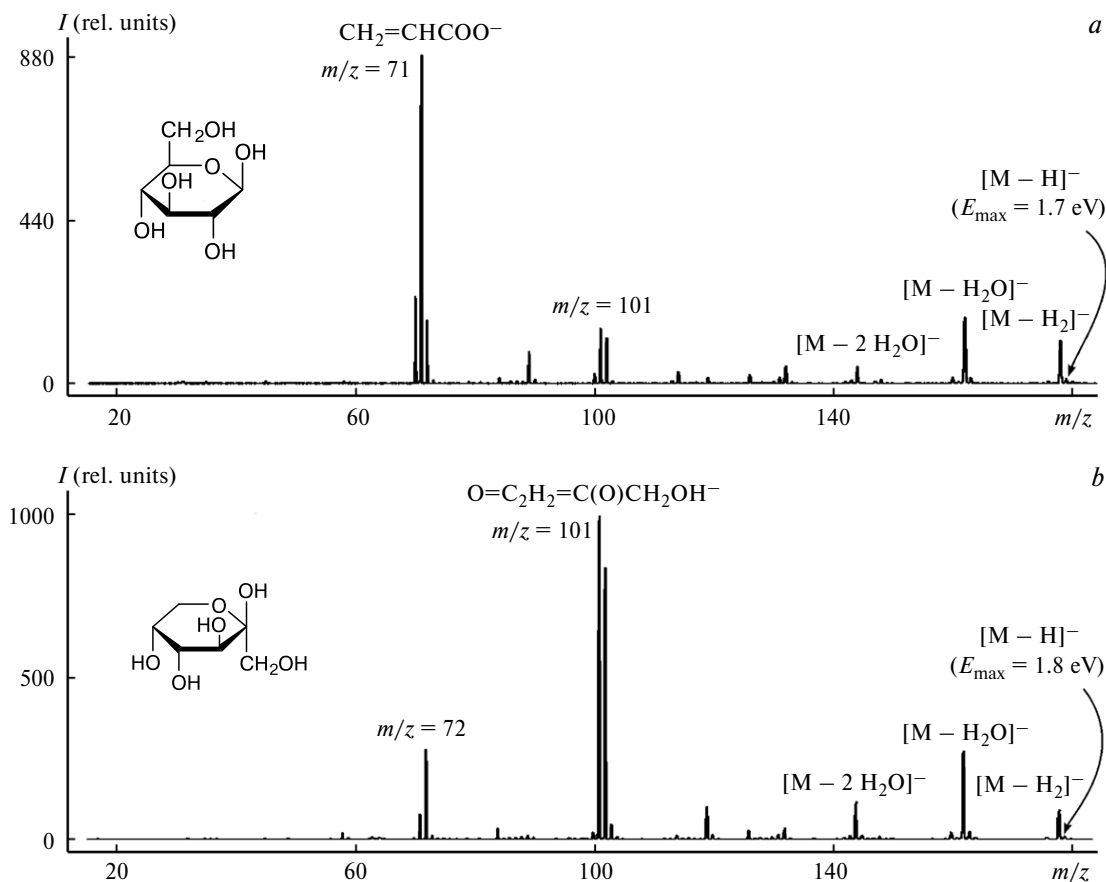


Fig. 8. Negative ion mass spectra of glucose (a) and fructose (b) ($\text{C}_6\text{H}_{12}\text{O}_6$) recorded at $E_e \sim 0.1 \text{ eV}$ (data were taken from Ref. 60). The electron energy resolution was 0.6 eV and the ionization chamber temperature was 108 °C for glucose and 78 °C for fructose.

individual mass-spectral profiles of isomeric compounds are averaged, which justifies the use of the SIM mode. It is PCDD, as the class of chemical compounds, that is characterized by the most complicated, labor-consuming, and expensive sample preparation procedures and analyses.^{284,358}

Studies of unsubstituted dibenzo-*p*-dioxin and its mono-, di-, tri-, and tetrachloro derivatives (MCDD, DCDD, TriCDD, and TCDD, respectively) revealed rich and characteristic REC NI mass spectra.^{39,54,127,195} No peaks of negative molecular ions were observed in the mass spectra of dibenzo-*p*-dioxin, MCDD, and DCDD.^{54,127} Earlier, it was believed that only PCDD molecules containing at least four chlorine atoms have positive electron affinities. Indeed, the mass spectra of TCDD isomers at thermal E_e exhibit a strong M^- peak (Fig. 9). However, a barely distinguishable M^- peak was also observed in the mass spectrum of 2,3,7-TriCDD,³⁹ thus indicating a positive EA_a of the molecule, which was also confirmed by the results of quantum chemical calculations.³⁵⁹

At $E_e < 6 \text{ eV}$, the yield of fragment ions from benzene and PAH is low or no fragmentation occurs at all.^{54,261} In

contrast to this, in the case of dibenzo-*p*-dioxin, the presence of heteroatoms (oxygen) opens various channels for fragmentation at $E_e \sim 4\text{--}5 \text{ eV}$; this also concerns all chloro derivatives of this compound. The $[\text{M} - \text{H}]^-$ peaks observed in this energy range can serve a secondary identification feature when determining the molecular weight of compounds. Chlorination causes the appearance of intense peaks of Cl^- ions in the NI mass spectra of dibenzo-*p*-dioxin derivatives. The maximum yields of these ions at $E_e \sim 0\text{--}1 \text{ eV}$ correlate with the total number of chlorine atoms in the molecules. The presence of Cl^- ions is an important indicator of chlorine-containing compounds, which is also used by highly sensitive Cl-specific detection techniques.²⁴⁰ Regioselectivity of formation of Cl^- ions from PCDD molecules under the REC conditions was studied.³⁶⁰ The EYCs of the $^{35}\text{Cl}^-$ ions and negative molecular ions formed from 1,2,3,4-TCDD and the corresponding intensity ratios corrected for the isotope distribution are consistent with the more recent results¹²⁷ (see Fig. 9, c).

An analysis of the absolute cross-sections of formation of fragment NI from PCDD molecules demonstrated that fragmentation mainly occurs through elimination of the

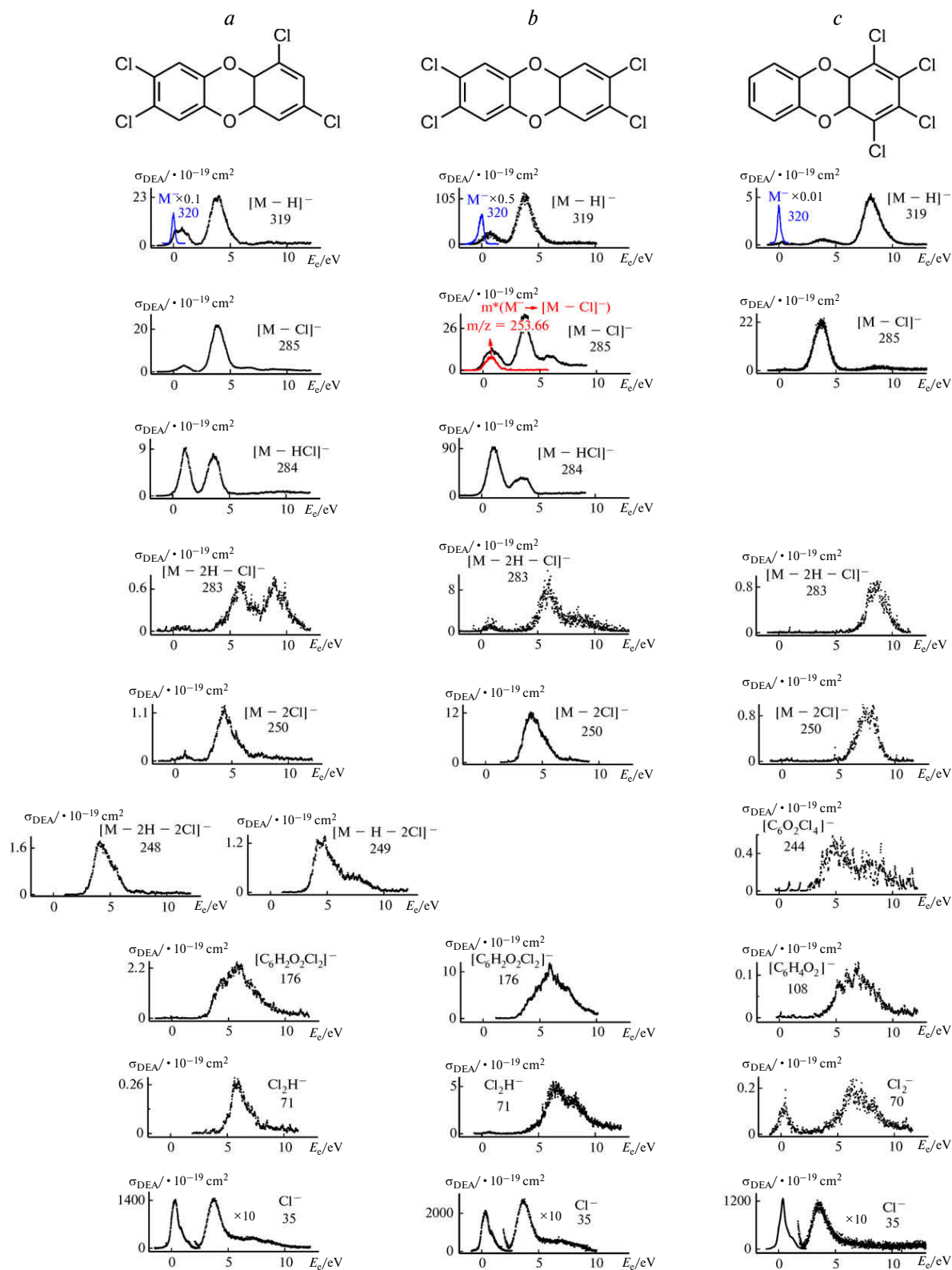
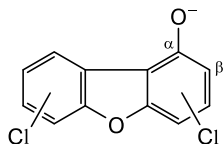
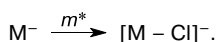


Fig. 9. Cross-sections of formation of each type of negative ions (with inclusion of contributions from all isotopic peaks) plotted vs. electron energy for tetrachlorinated isomers of dibenzo-*p*-dioxin: 1,3,7,8-TCDD (*a*), 2,3,7,8-TCDD (*b*), and 1,2,3,4-TCDD (*c*).¹²⁷ Conditions: direct inlet, electron energy distribution at half-maximum (FWHM) $\Delta E_{1/2} = 0.3\text{--}0.4$ eV, temperature of ionization chamber 100–110 °C; numbers denote the *m/z* ratios of the main isotopic peaks.

α -atoms (nearest to the oxygen atom). A thermochemical study⁵⁴ showed that abstraction of H_α and Cl_α atoms can be followed by a rearrangement, *viz.*, migration of oxygen atom to the α -position with the formation of energetically favorable oxyanionic dibenzofuran system.



This not only provides an explanation for the fact that the peak of $[M - Cl]^-$ ions formed from 1-MCDD in the resonance at $E_e \sim 4\text{--}4.5$ eV is nearly 50-fold more intense than the peak of $[M - Cl]^-$ ions formed from 2-MCDD, but also makes it possible to discriminate between these isomers with certainty. By analogy, the formation of Cl^- ions from 1-MCDD at $E_e 0\text{--}1$ eV is five times more efficient than the formation of Cl^- ions from 2-MCDD. The presence of Cl atom in the neighboring β -position catalyzes elimination of the α -atoms. For instance, in 2,3,7,8-TCDD four hydrogen atoms are surrounded by oxygen and chlorine atoms and the formation cross-sections of the $[M - H]^-$ and $[M - HCl]^-$ ions from 2,3,7,8-TCDD are maximum, whereas the formation cross-sections of the same ions from 1,2,3,4-TCDD containing no such hydrogen atoms are minimum among all PCDDs studied (see Fig. 9). Close arrangement of H and Cl atoms predetermines a rearrangement involving elimination of HCl molecule and Cl_2H^- cluster anion. This follows from the mass spectra of all PCDDs studied except 1,2,3,4-TCDD where H and Cl atoms are not appropriately arranged and the mass spectrum exhibits a Cl_2^- peak (see Fig. 9). A complete suppression of the formation of $[M - 2 Cl]^-$ ions at $E_e = 4$ eV is one more distinctive feature of 1,2,3,4-TCDD compared to the other two isomers of TCDD (see Fig. 9). The distribution of chlorine atoms between two parts of the dibenzo-*p*-dioxin molecule can be assessed from the composition of $C_6H_xO_2Cl_y^-$ ions formed upon elimination of a benzene ring. Although the mass spectra of isomeric 2,3,7,8-TCDD and 1,3,7,8-TCDD differ slightly, a significant relative intensity difference between the $[M - HCl]^-$ peaks with maxima at $E_e = 1$ eV is suitable for discrimination between these compounds. In addition, the mass spectrum of 2,3,7,8-TCDD exhibits a peak of metastable ions corresponding to dechlorination process (see Fig. 9, b):



The regularities of the REC NI mass spectra of PCDDs can underlie new analytical procedures or at least be used to improve the available related NI MS techniques.

Determination of the chemical composition of mixtures without preliminary fractionation

Complications associated with preliminary chemical and/or chromatographic separation of mixtures often prompt researchers to determine their composition by direct injection of samples into the mass spectrometer. A conventional analysis of multicomponent mixtures by low-resolution EI PI MS presents considerable difficulties. If the mass spectrum of each component of the mixture recorded at a primary electron energy of 70 eV has a complex pattern *per se*, the full mass spectrum will represent a "palisade" of peaks and each peak can be composed of the contributions from both molecular and fragment ions. In this context, REC NI MS is perfectly suited for solving the tasks in hand. Owing to resonant dependence of ion formation the maximum yields of ions from different compounds are observed in the REC NI mass spectra at different electron energies, so the assignment of peaks to a certain component of the mixture is not a challenge. Negative molecular ions are almost always observed at thermal energies E_e , while fragment NI are rarely formed under such conditions. Therefore, mass spectra recorded using any technique including ECNI MS are rather informative in the determination of the composition of even such complex mixtures, as crude oils;^{138,361–363} note that compounds invisible to PI mass spectrometry can also be identified.⁷⁷

Resonant electron capture NI MS seems also to be promising for quantification of the compositions of mixtures of structurally similar compounds, where ions from each component are formed with equal efficiency. For instance, Fig. 10 presents the mass spectra of a mixture of trifluoromethylfullerenes $C_{60}(CF_3)_n$.^{40,43} The available amount of the mixture was too small for separation of individual components by preparative chromatography. The PI mass spectrum (Fig. 10, a) demonstrates peaks corresponding to $0 \leq n \leq 10$. The most intense peaks correspond to even n values and can be tentatively assigned to molecular ions. This assumption is confirmed by the NI mass spectra recorded at $E_e \approx 0$ eV, which exhibit only peaks corresponding to the even n values. The NI mass spectra recorded at higher energies display predominance of peaks corresponding to odd n values and confirming their attribution to ions of fragment origin (Fig. 10, b).

The major component of the mixture (see Fig. 10) is a compound with $n = 6$, while the content of other components in the NI mass spectrum (at $E_e \approx 0$ eV) obeys a symmetric bell-shaped distribution. The pattern of the PI mass spectrum suggests that the bell-shaped distribution is shifted toward components characterized by smaller n values, which is likely due to distortion of the intensities of the $C_{60}(CF_3)_n^+$ peaks due to the contributions of the fragment ions formed from the components containing

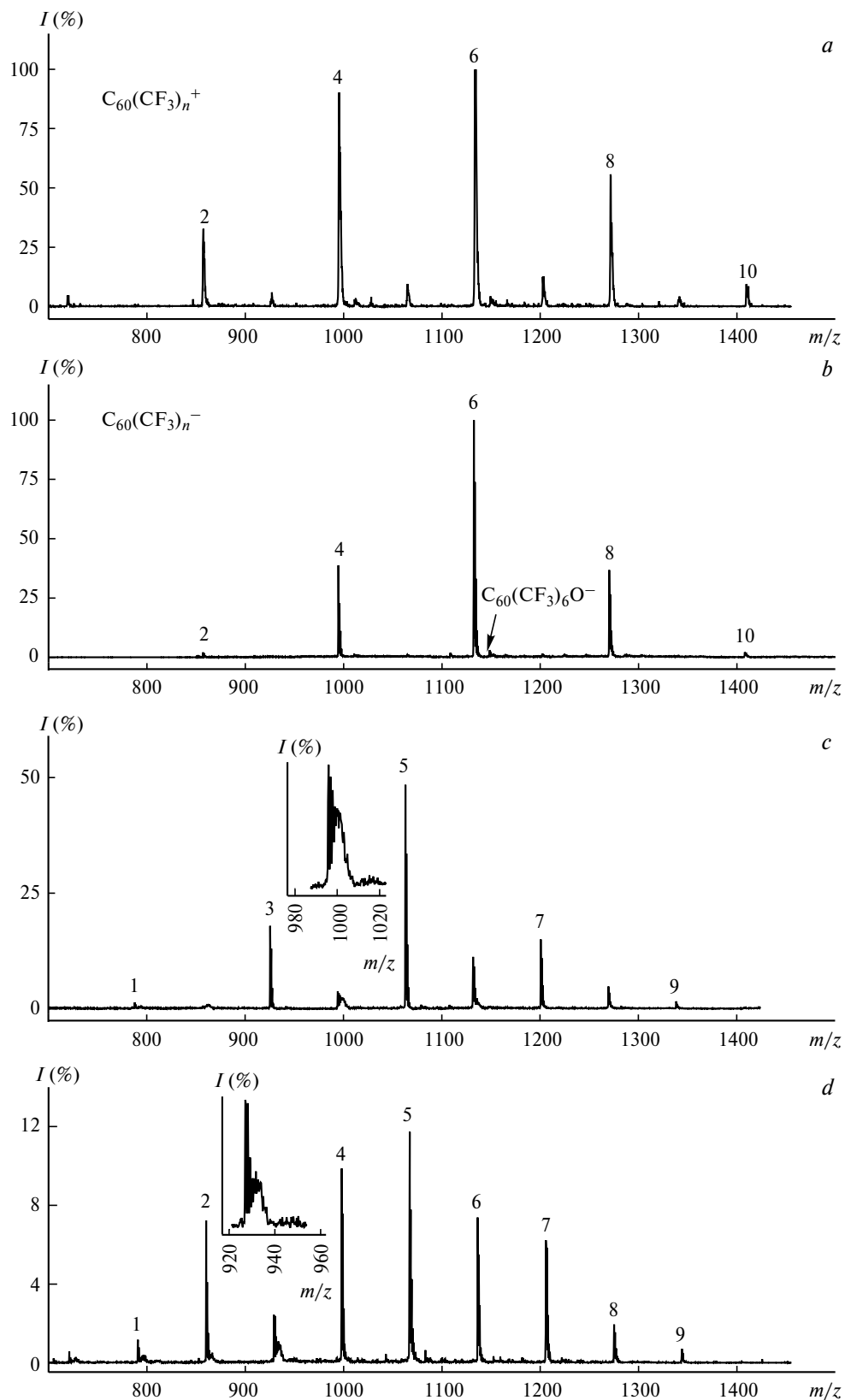


Fig. 10. Electron ionization PI (a) and REC NI (b–d) mass spectra of a mixture of trifluoromethylfullerenes $C_{60}(CF_3)_n$.⁴⁰ Insets: regions with metastable NI peaks corresponding to detachment of CF_3 group;⁴⁰ electron energy E_e/eV : 70 (a), 0 (b), 6.3 (c), and 10 (d); number (n) above the peak are in the range from 0 to 10.

a larger number of CF_3 ligands. Note that an analysis of the composition of this mixture using other ionization techniques (MALDI and ESI)⁴³ gave even more contradictory results since the mass spectra were not only distorted by fragmentation products of the initial components, but also complicated by the appearance of peaks of oxidized adducts formed in the course of the analysis.

Resonant electron capture negative ion mass spectrometry: selectivity of the method

Resonant (energy-dependent) nature of the formation of NI in electron-molecule collisions, strong dependence of the REC cross-section on the type of analyte molecules, and fragmentation of negative molecular ions obeying symmetry rules and thermochemical limitations underlie three aspects of selectivity of REC NI MS.

1. A distinctive feature of the method is high sensitivity to more electrophilic compounds and their fragments, which allows one to separate them from other substances. Predominance of characteristic ions of electron-withdrawing fragments (Hal^- , CN^- , NO_2^- , OH^- , etc.) in the mass spectra recorded at low energies E_e can also be treated as selectivity to entire families (classes) of chemical compounds.

2. Ions are formed only at particular electron energies (resonances) characteristic of a given compound, which allows one to selectively record a 2D NI mass spectrum of a sample by tuning the energy E_e .

3. Since the formation of particular NI from a given resonance is symmetry prohibited, and the thermochemical thresholds of dissociative decay following certain channels are also different, fragmentation of NI also appears to be selective to the molecular structure.⁹⁴ Specific selectivity of DEA fragmentation channels, complementary to those in traditional methods for sequencing peptides was also studied.^{46,47,78}

Multiple selectivity of REC NI MS is an undoubted advantage of the analysis of complex mixtures since it allows one to selectively detect and identify compounds belonging to particular classes, excluding the influence of secondary substances (less electrophilic ones or forming no NI) at a given electron energy. It is selectivity of REC NI MS in the analysis of PAH,^{25,65,291} organohalogen ecotoxicants, pesticides, herbicides,^{39,65,117} *N*-heterocyclic,⁶¹ hydroxyl- and carbonyl-containing agrochemicals,¹⁸⁵ antioxidants,^{298,327} pharmaceuticals,^{186,231} halocarbons,^{364,365} nitroaromatic explosives,^{75,89,307} organophosphorus CWA,^{83,87,366} and many other natural and synthetic compounds.^{10,116} that underlies the repeatedly mentioned usability of the method.

The selectivity of REC NI MS to electrophilic compounds was demonstrated⁸⁹ taking a GC/MS study of a mixture of toluene containing xylene impurity and a number of nitroaromatic compounds dissolved in acetone

in equal weight concentrations (Fig. 11) as an example. The explosive capacity of nitroaromatic compounds is known to enhance with increasing the number of nitro groups in their molecules. The total ion current chromatograms recorded in the PI mode (EI, $E_e = 70$ eV) show that the intensities of the peaks corresponding to toluene and xylene are more than tenfold higher than those of the peaks corresponding to dinitrobenzene and nitrotoluenes. When recorded in the NI mode (REC, $E_e = 4$ eV), the total ion current chromatograms demonstrate no toluene and xylene peaks. Probably, the electron energy chosen differs from the characteristic resonance energies and(or) the REC cross-section is too small. Note that the intensities of chromatographic peaks of nitrobenzene increase with the number of nitro groups in the molecules, that is, as the electrophilicity (EA_a) of molecules increases. Therefore, in these experiments the sensitivity of REC NI MS to 2,4,6-trinitrotoluene (TNT) is at least as high as that of EI PI MS (see Fig. 11). Such a selective sensitivity of REC NI MS, which can be controlled by varying the electron energy, should be used for the detection of hazardous substances, in particular, explosives.

3. Structural and analytical studies using commercially available mass spectrometers operating in the REC mode

At present, mixtures of low-molecular-weight compounds are usually analyzed using a combination of GC and EI PI MS (at $E_e = 70$ eV). The advantages of EI PI MS include high sensitivity and, as a consequence, the possibility to reliably identify small (including picogram) amounts of analytes. However, molecular positive ions are observed not for all compounds,³¹⁷ which complicates the determination of the molecular weight and identification of compounds. Among drawbacks of EI PI MS, there are a large number of peaks in the mass spectra (due to deep fragmentation of molecules; this hampers identification of compounds with close times of chromatographic retention) and difficulties in discrimination between isomers since their mass spectra are often identical to each other. The situation can be resolved using additional methods of investigation, e.g., IR, UV, and NMR spectroscopies. Note that most problems mentioned above can be solved by switching on the NI mode without essential modification of basic configurations of the available GC/MS instruments.

Like EI PI MS, REC NI MS is based on electron impact, but the electron energies are low ($0 < E_e < 15$ eV). It is this feature that allows one to implement the key capabilities of the title method with ease, although in somewhat simplified manner, using basic configurations of commercially available GC/MS instruments by simply changing the polarity and by properly setting up the operating mode. To save the cathode from burnout when

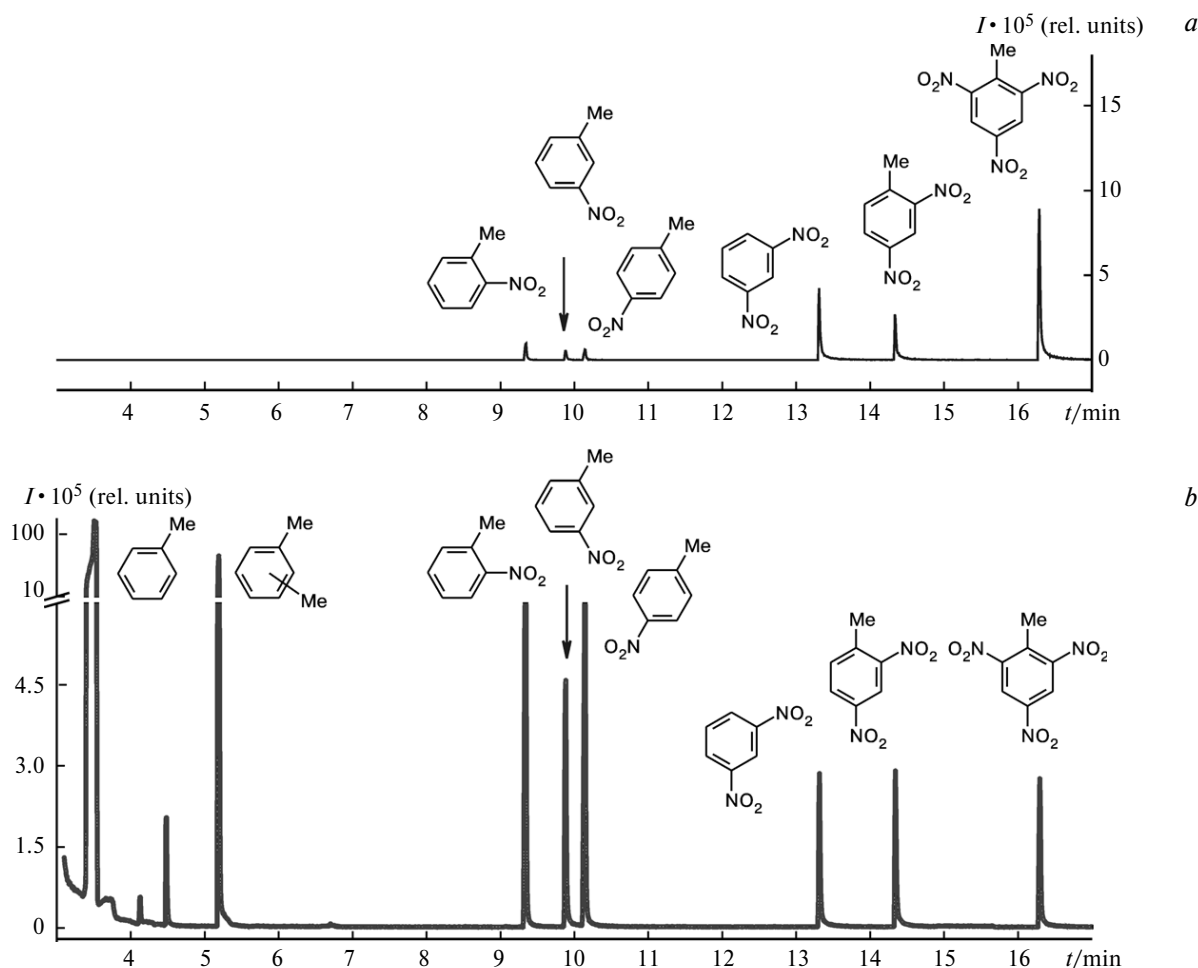


Fig. 11. The total ion current chromatograms of a mixture of toluene containing xylene impurity and a number of nitroaromatic compounds (100 ppm) in acetone (100 ng of each analyte in 1 μ L sample) obtained using REC NI MS ($E_c = 4$ eV) (a) and EI PI MS ($E_c = 70$ eV) (b).⁸⁹

decreasing the electron energy, it is strongly recommended to stabilize the cathodic current rather than use the standard electron current stabilization mode.¹¹⁸ Otherwise, if such a stabilization mode is not supplied by the manufacturer, one should use an appropriate external d.c. power supply that is connected to a break in the cathode circuit of the mass spectrometer.^{80,367} This undocumented "negative-ion" mode*¹¹ allows one to extend the standard capabilities of the instruments and to obtain additional analytically significant data at minimum expenses. In this connection the intentional development of methods for efficient utilization of the available analytical equipment in order to combine GC with both PI and NI MS seems to be reasonable. Clearly, success can be achieved only when based on fundamental knowledge of specific features of NI.

*11 Usually, this option is called "negative chemical ionization mode". The mode can also be switched on without corresponding replacement of basic configuration modules.

Note that most commercially available GC/MS instruments can be equipped upon request with the option of a chemical ionization which includes a special type of ion source, additional compressed gas and vacuum equipment, and the possibility to record NI mass spectra. Thermal electrons appear as a result of collisions between high-energy primary electrons ($E_c \sim 100\text{--}500$ eV) and molecules of a reagent gas that also serves a buffer (thermalizing) agent and the source of secondary electrons detached as a result of ionization. Often, literally following the analogy (see Refs 358 and 368) with conditions for chemical ionization PI MS and without dwelling on details of processes under study, ECNI MS (see Refs 18 and 369) is still incorrectly named negative chemical ionization (NCI).^{110,284,370,371} The capture of thermal electrons, which is characteristic of only electrophilic compounds, allows one to obtain NI mass spectra that usually exhibit a single strong peak of M^- ions. Fragmentation and analysis of non-electrophilic compounds can be realized at specified non-thermal energies E_c in the range of

0–15 eV that can be controlled only under rather high vacuum in the IC of the instrument, *i.e.*, under the conditions that are atypical of chemical ionization.

Applicability of commercially available GC/MS instruments: substantiation

Basic configurations of commercially available GC/MS instruments are designed for highly efficient generation and detection of positive ions in the EI mode. Unlike the instruments modified for operation in the REC NI mode, a standard ion source of the mass spectrometric detector of a GC/MS instrument is not optimized for generating ions at $E_e < 15$ eV. Nevertheless, the basic design of conventional GC/MS instruments enables a controlled decrease in electron energy and thus rather efficient generation of NI in the REC mode. As far as we know, the first publication concerning REC NI MS with GC separation dates back to 1991.³⁷² When the analyte is introduced into the IC *via* a GC column, a question arises as how NI appear, *viz.*, as a result of direct electron attachment or by attachment of the secondary electrons that lose their energy in collisions with the IC walls or with atoms of the carrier gas (helium). Helium, which is used as carrier gas for GC, is also treated as good buffer gas.³⁶⁸ However, experimental studies^{79,80} carried out using a GC/MS instrument comprising a Chromatec Crystal 5000.1 gas chromatograph (JSC SDO Chromatec, Yoshkar-Ola, Russia) and a Finnigan DSQ quadrupole mass spectrometric detector (Finnigan, USA) with a variable-energy electron beam (initially, these were low-energy electrons) showed that the NI formation processes in the IC of the quadrupole mass spectrometer can to a good approximation be described as REC with controlled energy while thermalization of electrons is insignificant.

This statement is based on the results of a comparative analysis of the NI mass spectra of a mixture of chlorophenol isomers, recorded using a magnetic sector mass spectrometer equipped with a direct inlet system and a quadrupole mass spectrometer with a GC inlet system. In the latter case, a short-term appearance of chromatographic peaks precludes recording the effective yield curve of NI for each component of the mixture while scanning the electron energy E_e . Therefore, the experiments were multiply repeated and the NI mass spectra were recorded at different fixed energies E_e varied with an increment of 1 eV. For each component of the mixture, the intensities of the NI peaks were plotted point-by-point above the "reference" NI EYCs obtained using the magnetic sector mass spectrometer modified for operation in the REC NI mode^{55,56} (Fig. 12).

Although no exact coincidence was obtained, the two data sets correlate. By and large, positions of resonance peaks of the EYCs on the energy scale agree with one

another (taking account of an error of ± 0.5 eV introduced by the design of the quadrupole mass spectrometer). This gives no reason to doubt the origin of the observed NI, *viz.*, they mainly appear as a result of resonant capture of just the primary electrons with controlled energy rather than the secondary electrons. Probably, the latter process can also contribute, but this contribution is negligible. This can be substantiated by slightly increasing trend in the intensities of most NI peaks with increasing E_e . The effect is typical of the capture of (secondary) electrons that lost their energy in collisions with IC walls or with the analyte molecules (so-called "scavenger effect").^{56,373}

The aforesaid suggests that helium used as thermalizing agent under conditions of routine GC/MS experiments plays a significant role only at high energies of primary electrons, while at low electron energies it is of minor importance (at least at those helium concentrations that are necessary for standard operation of the GC/MS instrument). The loss of electron energy through inelastic collisions in atomic helium is known to be possible only at $E_e \geq 19.35$ eV.^{142,373} Indeed, helium appeared to be the least efficient moderating gas³⁷⁴ while electron thermalization was much more efficient using molecular gases (N_2 , CH_4 , CO , CO_2 , NH_3 , *etc.*) It is quite probable that the conditions for single collisions in the IC of the GC/MS instrument are not met; however, the reproducibility of the entire set of "reference" mass spectra (see Fig. 12) allows one to conclude that this is insignificant for mass spectrometric analysis in the REC mode. Helium as buffer gas can still act as coolant stabilizing NI.^{374,375} However, it is important to bear in mind that the efficiency of cooling will unavoidably decrease with increasing temperature of the capillary column during the chromatographic run, which can strongly influence the intensities of temperature-dependent NI peaks.

An analysis of broad profiles of resonance peaks (see Fig. 12) suggests that distinctions between the NI EYCs and the "reference" ones are due to a large scatter of electron energies (low resolution). Indeed, the design of the IC for operation in the EI PI mode is optimized to attain high sensitivity of the instrument rather than to correctly operate with low-energy electrons and to generate NI in the REC mode. Nevertheless, the wide energy distribution of ionizing electrons appears to be useful for analytical purposes when recording a conventional mass spectrum at fixed E_e value, since it allows one to cover wide resonance peaks or even a number of close-lying resonances from which ions of different weight are formed. In spite of reduced selectivity of ion formation with respect to E_e , the wide energy distribution leads to an increase in the total intensity of ion formation and thus the sensitivity of the instrument and allows one not to miss the possible formation of characteristic NI (which is of importance for structural studies), thus

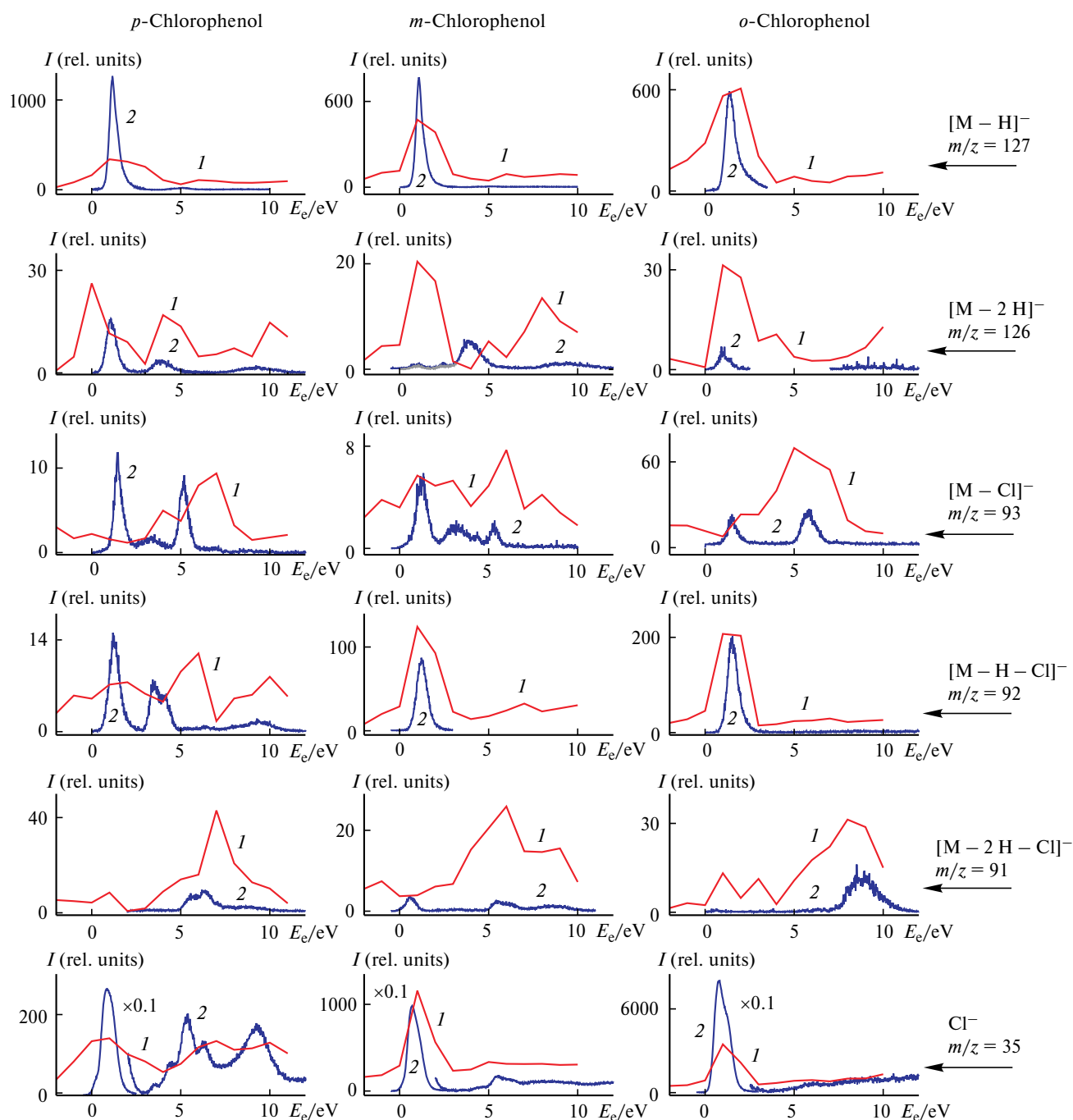


Fig. 12. Effective yield curves of NI of chlorophenol isomers obtained with a Chromatec Crystal 5000.1/Finnigan DSQ GC/MS instrument (1) and a modified MI-1201V magnetic sector mass spectrometer (2) (adapted from Ref. 79).

eliminating the need for recording additional mass spectra at other energies E_e .

Summing up, REC NI mass spectra can be obtained using a commercially available GC/MS instrument not equipped with an electrons monochromator. This allows one to carry out mass spectrometric analysis in the mode that is procedurally indistinguishable from the standard operating mode of the mass spectrometer.

Organophosphorus compounds

Organophosphorus compounds are known first of all as CWA and pesticides.^{376,377} Characteristics of the most common representatives of this class of chemical compounds were determined using traditional methods of analytical chemistry; methods for the detection and identification of the compounds in question and products of

their transformations were developed and tested, and corresponding databases were compiled.^{378–380}

Investigations of organophosphorus compounds by REC NI MS began with a study of pesticides.²¹ Most studies were carried out using a JEOL DX-300B mass spectrometer equipped with a tailor-made TEM. It was established that fragmentation of negative molecular ions of parathion (thiophos) can proceed (i) through dissociation of the bond between the phosphorus atom and the oxygen atom bonded to the benzene ring and (ii) through the formation of an intermediate bond between the sulfur atom and a carbon atom from the π -system followed by elimination of a fragment NI. The appearance energies of negative molecular ions and fragment ions for eight parathion analogues were determined. More recently,³⁰ the effect of the buffer gas (helium) pressure on the intensity and composition of ions being formed was revealed.

A fragmentation study⁶⁵ of NI of organophosphate pesticides using the results obtained in Ref. 381 made it possible to construct an appearance map of fragment ions at different energies E_c and to demonstrate the variety of fragmentation pathways upon variation of the electron energy.

A series of studies^{81,83,87,88} of phosphoric acid esters was carried out using a modified³⁶⁷ commercially available Chromatec Crystal 5000.1/Finnigan DSQ GC/MS instrument. It was shown that the 2D REC NI mass spectra recorded at a fixed energy E_c significantly improve the reliability of identification. A fragmentation study⁸¹ of *O*-ethyl-*S*-2-(*N,N*-diisopropylamino)- and *O*-isobutyl-*S*-2-(*N,N*-diethylamino)ethyl methylthiophosphonates belonging to the most toxic CWA (V-gases) revealed that the process can proceed *via* dissociation of the C—O or C—S bond with retention of the negative charge on the phosphorus-containing fragment. The NI mass spectra also demonstrated peaks of deprotonated molecular ions whose intensities were less than 5% of the intensity of the main peak in the mass spectrum. Fragmentation of other CWA (*O*-isopropyl methylphosphonofluoridate (sarin) and *O*-pinacolyl methylphosphonofluoridate) proceeds analogously.⁸³ The appearance of peaks of deprotonated molecular ions was also observed.

A study⁸⁸ of mono- and dichlorophosphates revealed specific features of fragmentation of corresponding negative molecular ions and it was shown that the process mainly proceeds *via* dissociation of the C—O bond followed by elimination of alkoxy radical. The NI mass spectra also exhibited peaks of molecular and atomic chlorine. A salient feature of the fragmentation of dichlorophosphates is the absence of peaks of deprotonated negative molecular ions.

The Chromatec Crystal 5000.1/Finnigan DSQ GC/MS instrument was also used to study tetraalkyl pyrophosphates, *O*-trialkyl phosphates, and phosphonates.⁸⁷ Interestingly, fragmentation of negative molecular ions of

tetraalkyl pyrophosphates involves elimination of only one *O*-alkyl radical and the number of carbon atoms in this species has little effect on the preferred elimination pathway. Therefore, in this case the "loss of the largest alkyl radical" rule used in PI MS, is invalid. The NI mass spectra of pyrophosphates containing various alkyl substituents exhibit peaks corresponding to elimination of each radical. Taking account of the very low energy resolution (E_c) of the equipment, exact determination of the resonance energies was impossible. Nevertheless, all publications^{81,83,87,88} reported that the experimentally determined energy E_c corresponding to the maximum ion current signal was about 4 eV.

Studies^{81,83,87,88} demonstrated high efficiency of joint use of complementary data obtained by EI PI MS and REC NI MS for structure determination of the substances under investigation and substantiated the appropriateness of introducing REC NI MS into analytical practice. Using the data obtained by both methods realized on the same analytical instrument, methods were developed for the determination of the number of carbon atoms in alkyl radicals formed from V-gases, pyrophosphates, and phosphates.

Studies of phosphates illustrated one more undoubted advantage of REC NI MS as analytical tool, *viz.*, a small number of lines in the mass spectra and, therefore, the possibility to predict them and ease in interpreting the results obtained. Indeed, fragmentation of organophosphorus compounds produces a few fragment NI through simple dissociation of the weakest bond (usually, the O—Alk bond for alkoxy compounds) and elimination of the neutral (alkyl, pyrimidyl, pyrophosphonate) oxo substituent as the entire fragment from negative molecular ions. The corresponding fragmentation pathways are consistent with the energy characteristics obtained from quantum chemical calculations,⁸³ which allows one to predict the ion composition of the mass spectra of those compounds with a reasonable accuracy. Moreover, the NI mass spectra can be predicted reliably using an empirical algorithm based on the experimental data for a small number of homologues of this group of compounds. The mass spectra of the compounds not included in the training set were generated by the algorithm and the similarity between the simulated and experimental mass spectra by the forward and reverse search were more than 750 units.⁸³

Nitroaromatic compounds

Nitro compounds are of interest since they represent components, degradation products, or precursors of explosives. Research into this class of compounds aimed to support counter-terrorism efforts remains topical.

Usually, explosives are detected and identified by GC and an electron capture detector,³⁸² an ion mobility increment spectrometer,³⁸³ and other non-mass-spectrometric

methods.³⁸⁴ The REC NI MS studies of nitroaromatic compounds (mainly nitrobenzenes and nitrotoluenes including other explosives) were carried out by different research groups. The authors of a study⁷⁵ reported as long as 1972 claimed the possibility of using NI mass spectra to identify TNT. To detect TNT vapors in airline baggage, it was proposed to design a small mass analyzer focused at m/z 46 (nitro group) at $E_e = 6$ eV (main peak in the NI mass spectrum).

It was shown⁶⁸ that six nitro compounds (*o*-, *m*-, and *p*-nitrophenol; *o*-, *m*-, and *p*-nitroaniline) form long-lived negative molecular ions that can be detected using a TOF mass spectrometer.

A hemispherical electron monochromator was used³¹² to study the formation of NI from three isomers of dinitrobenzene. Fragment NI formed from those compounds, the resonance energies, and possible fragmentation pathways were studied in detail in the energy range $0 < E_e < 10$ eV. The possibility to identify the isomers in hand and to discriminate between them was also demonstrated.

Strong fragmentation of negative molecular ions from TNT was thoroughly studied using a quadrupole mass spectrometer equipped with a hemispherical electron monochromator and direct inlet of vaporized samples.³⁸⁵

A comparative study³⁸⁶ on resonance processes in the TNT, 1,3-dinitrobenzene, and (4-*tert*-butyl)-2,6-dimethyl-3,5-dinitrophenylethan-1-one (musk ketone) molecules is also of interest. High-purity samples of these compounds were studied using two instruments, *viz.*, a quadrupole mass spectrometer with high electron energy resolution and a high-mass-resolution, two-sector magnetic mass spectrometer equipped with a standard Nier-type ion source with low electron energy resolution. The authors thoroughly studied fragmentation of negative molecular ions of musk ketone at different electron energies and proposed to utilize REC as highly sensitive and selective tool for the detection of explosives.

Researchers from that group also investigated and identified dinitrobenzene isomers as degradation products of TNT.⁴⁸ They established the fragmentation pathways of the isomers of dinitrobenzene, confirmed them by quantum chemical calculations, as well as discriminated between the isomers and determined the energy ranges corresponding to the resonances and the m/z ratios of the fragment ions characteristic of these compounds.

A mixture of two explosives, hexogen (RDX) and pentrite (PETN), was studied³⁸⁷ and the EYCs were recorded at different electron energies for the nitro group (m/z 46) as the main fragment NI. The authors of that study proposed to use individual EYCs to identify pure compounds.

There are two points common to all these NI MS studies of nitro compounds. The key point is the use of the direct inlet system (no chromatograph) and, as a conse-

quence, impossibility to analyze a mixture of substances. The other point is utilization of an additional device, *viz.*, an electron monochromator. Nevertheless, it was repeatedly concluded that REC NI MS is highly sensitive to electrophilic compounds and applicable to analysis of nitroaromatics.

The potential of REC NI MS for analysis of a mixture of nitro compounds was demonstrated in a comparative study⁸⁹ taking a group of compounds including toluene, three isomers of nitrotoluene, 1,3-dinitrobenzene, 2,4-dinitrotoluene, and TNT as examples. These compounds were identified by EI PI MS and REC NI MS using a basic configuration of a Crystal 5000.1/Finnigan DSQ GC-MC instrument. Liquid samples of mixtures with different concentrations of analytes in the solvent were introduced *via* a gas chromatograph. Preliminary experiments made it possible to determine the electron energy and the resonance energy range to obtain a maximum analytical signal in the NI mode. To this end, a dosed amount of TNT was repeatedly introduced into the chromatograph and the energy of ionizing electrons was successively increased from 0 to 10 eV with an increment of 1 eV at every run.^{79,80} An analysis of the total ion current chromatograms revealed the most efficient formation of NI from TNT at $E_e \sim 4$ eV. It is this electron energy that was used in the subsequent REC NI MS experiments with all compounds. The cathode can be damaged when operating with low ionization energies; therefore, to save the cathode, it was heated with external power supply in the current stabilizing mode.³⁶⁷

The ion composition of the NI mass spectra of the model mixture is in reasonable agreement with the data obtained on other types of mass spectrometers (magnetic, quadrupole, TEM) for nitrophenols and nitrotoluenes,^{57,220,387,388} dinitrobenzene,^{48,312} and TNT.^{385,386} The peaks of NO_2^- , $[\text{M} - \text{NO}_2]^-$, $[\text{M} - \text{OH}]^-$, and $[\text{M} - \text{H}]^-$ ions are characteristic of all compounds. Weak M^- peaks were also observed in spite of non-thermal energy $E_e > 0$ eV, which is inappropriate for generation of these ions. Significant differences between the relative intensities of ion peaks in the mass spectra were explained by different electron energies chosen to record the mass spectra, different electron energy resolution, and different mass discriminating ability of specific instruments. The mass spectra recorded at the same energy E_e demonstrated good reproducibility. In particular, the similarity scores between the NI mass spectra retrieved from the home-made mass spectral database and the re-recorded experimental mass spectra were high.

The limits of detection of nitrotoluenes were determined in the experiments with mixtures of analyte solutions in acetone. The solutions (concentrations were 100, 50, 10, and 5 ppm in 1 μL sample) were introduced into a chromatograph. Experiments with each concentration were repeated at least five times. To compare the sensitiv-

ity of EI PI MS and REC NI MS, the experimental mass spectra and the mass spectra retrieved from databases (NIST database³⁵⁰ for EI PI MS and home-made ever-expanding "varhzbz" database³⁸⁹ for REC NI MS) were compared.⁸⁹ High values of similarity scores between the REC NI mass spectra of TNT and the mass spectra retrieved from the databases (at least 850 units) suggest high reliability of identification and are retained up to a concentration of 5 ppm (limit of identification is at most 5 ng). The corresponding results obtained for the EI PI mass spectra were 50 ppm (50 ng), thus indicating higher sensitivity of REC NI MS to TNT.

However, these results are way below those of a study³⁰⁷ carried out using a magnetic sector, double focusing mass spectrometer equipped with an electron monochromator for operation at $E_c \approx 0$ eV (in the energy range corresponding to the most efficient electron capture) in SIM mode. In this case, the limits of detection of explosives in the mixtures were of the order of 10^{-9} .^{*12} Nevertheless, experiments demonstrated the possibility to identify TNT using routine REC NI MS analysis on a commercially available GC/MS instrument and a higher sensitivity of REC NI MS compared to EI PI MS. This gives promise that further REC NI MS studies of other explosives containing a larger number of nitro groups may will also be topical.

Resonant electron capture negative ion mass spectrometry studies of organosulfur compounds

Organosulfur compounds are the most abundant components of crude oils and gas condensates after hydrocarbons. There is considerable literature on REC NI MS studies and determination of qualitative composition of crude oils from different deposits.

By and large, REC NI MS analysis of crude oils and gas condensates is similar to that of other classes of organic compounds. In the case of sulfur-containing compounds the role of markers is played by SO_2^- , SO_3^- , and HS^- groups^{390–394} (*cf.* nitro group for explosives). The so-called group identification, *i.e.*, the assignment to a particular class of organic substances, is based on the reliably determined energy of the resonance corresponding to the marker group. The yield of SO_2^- anions from alkyl-substituted sulfides, sulfoxides and sulfones, and cyclic polysulfides is maximum at $E_c = 3$ eV,³⁹⁴ 5 eV,^{390,391} and 1 eV,³⁹⁴ respectively. The chemical composition of such a complex mixture as crude oil can be determined without preliminary fractionation using the REC NI mass spectra recorded at thermal energies E_c .^{138,362,363} Compounds not detected in the PI mass spectra can appear in the REC NI mass

spectra.⁷⁷ A thesis¹³⁸ was defended, which summarized the results of analytical studies of organosulfur compounds by photoelectron and NMR spectroscopies, presented the results of REC NI MS investigations of more than 10 classes of chemical compounds including thiols, sulfoxides, sulfones, disulfides, *etc.*, and determined the energies of resonances and the characteristic ions. Experiments involved joint use of capillary GC and various detectors including an NCI MS detector. Of particular interest are such characteristics as the limit of detection and the limit of identification. It was found that REC NI MS is second to only GC/MS with selective ion detection. Therefore, one can expect improved efficiency of analysis of crude oils using GC/MS instruments operating in the REC NI mode which can be implemented with ease on modern commercial equipment.

Resonant electron capture negative ion mass spectrometry as a counterpart of classical EI PI MS

The title method can be used to obtain additional information on chemical substances which is inaccessible to EI PI MS. For instance, information on NI from small particles (CF_3 , NO_2 , CN , C_3F_6 , Hal, *etc.*) having high electron affinity and representing structural fragments of the vast majority of organic compounds greatly simplifies the interpretation of PI mass spectra. Such species are rarely detected in the PI mass spectra since usually they are eliminated as neutral fragments. In addition, the NI mass spectra of (electrophilic) compounds containing several electron-withdrawing groups can be more informative than the PI mass spectra, as is confirmed by the example shown in Fig. 13, and by the mass spectra of positive and negative ions formed from 1-fluoro-2,4-dinitrobenzene.⁸⁶

It was demonstrated^{87,88} that data obtained by EI PI MS and REC NI MS are complementary. The possibility of implementing both experimental techniques using the same instrument is a great advantage over any single analytical method. An analysis in the complementary (*e.g.*, REC NI) mode requires simply changing the polarity and putting the GC/MS instrument into operation to re-scan the same analyte. This avoids the obtaining of missing analytical information using other methods that can require a separate sample preparation procedure and can even be inaccessible at all under field-oriented conditions. Combining EI PI MS and REC NI MS allows one not only to significantly improve the reliability of identification of various substances, but also to solve the previously difficult tasks (*e.g.*, determination of the number of carbon atoms in the alkyl radicals of phosphates,⁸⁸ tetraalkyl pyrophosphates,⁸⁷ and *O*-alkyl-*S*-2-(*N,N*-dialkylamino)-ethyl alkylthiophosphonates^{81,84}) with ease.

*12 1 ppb = 10^{-9} .

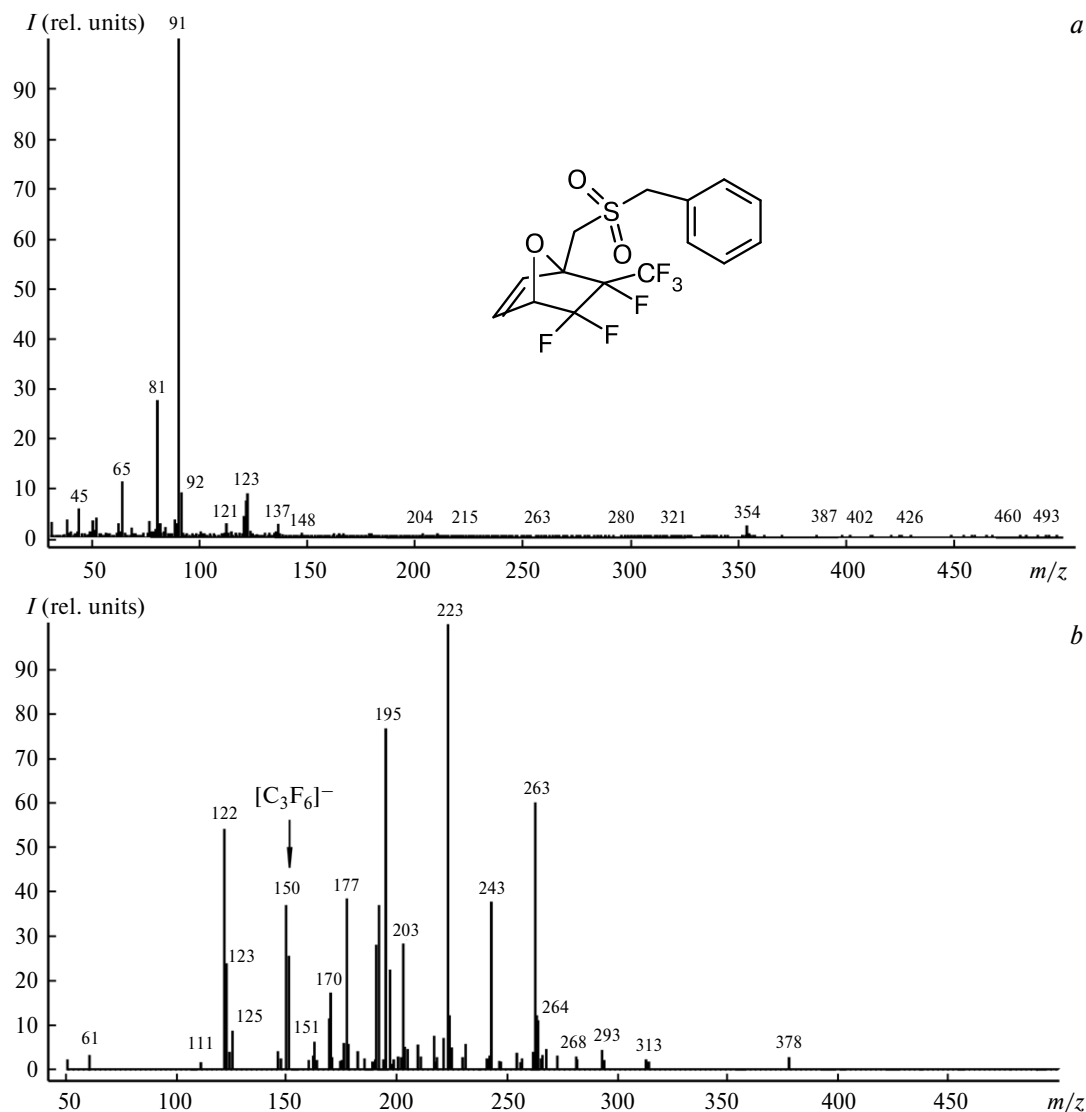


Fig. 13. Positive ion (a) and negative ion (b) mass spectra of 1-(benzylsulfonylmethyl)-5,5,6-trifluoro-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene.

Derivatization as a tool for improving the sensitivity of mass spectrometric identification

The ability of compounds to vaporization (or sublimation) without decomposition is of great importance for mass spectrometric analysis. Unfortunately, many substances, especially biologically significant compounds, undergo thermal decomposition at temperatures that are too low to sublime and to reach the desired vapor pressure. Exclusive experiments with thermally labile compounds can involve the use of a direct inlet tube and the introduction of (solid) samples directly coated onto the ionization chamber wall to prevent the sample from overheating. This technique was used to study oligopeptides,^{46,47,62} sugars and their derivatives (nucleosides),^{42,60,62,395} and many other biologically significant compounds.^{45,61,63,231,235}

Vaporization of the sample coated onto the surface of a rapidly heated wire placed close to the electron beam was used in a REC study of peptide fragmentation;⁷⁸ however, the procedure appeared to be labor-consuming and hardly suitable for routine analytical studies.

The volatility of hardly subliming and thermally unstable compounds can be increased by derivatization using the acylation, alkylation, silylation reactions, *etc.*^{396,397} For instance, highly volatile amino acid methyl esters were studied instead of the parent compounds.^{235,398} Attempts²⁶ to study a solid sample of 1,4,7,10,13,16-hexahydroxy-5,6,11,12,17,18-hexaazatrinaphthylene failed since the compound rapidly decomposed on heating prior to reaching an optimum sublimation temperature. However, it was established that the necessary vapor pressure at moderate heating temperatures can be reached using its derivative,

viz., 1,4,7,10,13,16-hexamethoxy-5,6,11,12,17,18-hexazatrinaphthylene whose mass spectrum was then successfully recorded (see Fig. 2).

Derivatization facilitates efficient GC separation. However, there is one more reason why it is of interest for progress of REC NI MS as analytical method. An important feature of REC NI MS is high sensitivity to electrophilic compounds. The electron affinity of molecules can be increased by introducing electron-withdrawing substituents. From this standpoint, there is considerable interest in the reactions involving reactants bearing a large number of electrophilic groups, such as fluorine atoms: pentafluoropropanol, pentafluorobenzene, *etc.* These promising practical applications of NI were reported in the literature^{9,30} while the efficiency of this approach was demonstrated^{399–401} in the detection of NI from the derivatives obtained under chemical ionization with methane. The results of studies on the search for and application of (mostly polyfluorinated) derivatizing agents for analysis of biomedical samples were generalized.¹¹⁴ Owing to occasional use of NI MS systematic search for new electrophilic derivatizing agents is rare to occur.

How to improve commercially available mass spectrometers and an outline of prospects for analytical applications of REC NI MS

Most REC NI MS studies carried out in the USSR and Russia used magnetic sector mass spectrometers modified in the laboratories for operation in the NI mode (see Section 1). Researchers abroad also employ home-made instruments that are usually based on quadrupole or TOF mass analyzers and equipped with an electron monochromator. At present, the available equipment and labor-consuming experiments are inappropriate for expansion as tools for routine analyses. In addition to the complex design there are methodological problems associated with specific features of the setting up procedure and with stability of the operation of the instruments with electron monochromator. Emphasize that researchers at Ufa group use this device only for high-precision measurements, so the necessity of electron monochromator for routine analytical studies^{21,29,30,117} is still a debatable issue.

For instance, a GC electron monochromator TOF mass spectrometer allows one to record 3D REC NI mass spectra at fast (to 80 kHz) scan of electron energy.²⁹ The authors of that study believe that the instrument will allow one to record the ion EYCs for the compounds under study and thus significantly increase the amount of analytical information during the time taken by routine GC analysis. By and large, the results of the primary tests appeared to be successful.³⁴ It was shown that the ion composition detected, the shape of the ion EYCs, and the resolution of the instrument vary insignificantly when rapidly scanning the energy E_e . However, some difficulties were

revealed, namely, the need for high-speed equipment and software for rapid recording of data streams containing a huge body of information stored in the mass spectra that represented in fact a 4D data array taking into account the chromatographic component. Probably, such a sophisticated equipment and specifics of the task (processing of large amounts of complex experimental data) will require much more high-skilled staff, which seems to be unfeasible for ordinary forensic and drug testing laboratories. That is why it's hard to expect wide dissemination of this R&D product.

We propose a technologically, methodologically, and organizationally simpler, less expensive, and more efficient method for making chromato-mass spectrometric analysis much more informative, *viz.*, combining the technological and methodological simplicity of EI PI MS with the advantages of REC NI MS to essentially improve the informativity of scientific research. In this review, we showed that even 2D REC NI mass spectra contain analytically significant information that is sufficient for the detection and identification of chemical compounds and determination of their structures. In addition, our idea can be realized at almost no extra cost using the available GC/MS instruments. This approach and its applicability to the solution of analytical tasks were reported recently.^{86,88,89}

The only bottleneck of our approach compared to EI PI MS is the need for preliminary experimental determination of the energies of resonances, *i.e.*, the optimum energies E_e for recording the most intense and (or) informative NI mass spectra. This requires multiple recording of mass spectra of a particular analyte in the energy range from 0 to 10–15 eV with an increment of 1 eV (this corresponds to a minimum discretization step for ionizing electron energy determined by the technical constraints of the most commercial mass spectrometers) followed by choosing the optimum E_e value based on the experimental results. This labor-consuming and rather long procedure can be replaced by the following.³¹⁵ By analogy with the developments^{21,29,123,127,272,313,314} we propose continuous recording of full mass spectra spanning the entire electron energy range of 0–15 eV synchronized with the yield of components from the chromatographic column. Since no electron sources with wide uniform electron energy distribution are available, we decided to use hardware-implemented rapid multiple scanning the energy E_e within the scanning time of the mass spectrum with synchronous summation of the ion signal being detected at a given value of the m/z ratio.^{85,316} Continuous scan of E_e in the range mentioned above allows one to with certainty cover all possible resonance peaks of ions of each mass formed from all low-molecular-weight compounds. Despite the loss of information on the energy of resonances upon integration of the ion EYCs, this method for recording NI mass spectra appeared to be rather efficient in the case of routine

analysis. First, the full mass spectrum includes peaks of all NI from a given compound irrespective of the parent resonance state including negative molecular ions. Second, the intensity of the total ion signal is higher than that of the signal recorded at a fixed energy E_c . Third, the fact that the REC NI mass spectra no longer depend on the electron energy E_c has beneficial effect on both inter-sample and inter-instrument reproducibility of the mass spectra. Fourth, the time taken by such a "broadband" recording of the NI mass spectra is comparable with the time required for quantitative recording of chromatographic peaks. Having thoroughly debugged the equipment (energy variation at a frequency of 750 Hz appeared to be insufficient, and a number of feasible problems posed, being associated with synchronization with the mass scanning) and standardized the technique for recording full REC NI mass spectra, one can expect nearly identical inter-instrument reproducibility (at the same temperature) as in the case of EI PI MS. This will allow one to design a public REC NI mass spectral database similar to the widely used Wiley and NIST databases and to develop and certify procedures for analysis of various classes of compounds.

Conclusion

Summing up, we demonstrated that a mass spectrometer operating in the REC mode represents a kind of an analytical laboratory that enables determination of the molecular weight, selective identification of individual compounds without preconcentration or separation, discrimination between isomers, detection of free radicals, determination of the thermochemical constants, electronic structure, and geometry of molecules and ions, detection and determination of submicroscopic amounts of chemical substances, obtaining full fragmentation patterns in the case of dissociative electron capture. The potential of REC NI MS and the application fields of the results obtained by this method are boundless just like as the number of chemical compounds to be studied and ever-increasing range of fundamental problems and structural and analytical tasks. Rational implementation of the potential and advantages of REC NI MS (see above) using modern equipment seems to be promising for improvement of the instrumentation of analytical chemistry and for general progress of physical chemistry.

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This work does not involve human participants and animal subjects.

The authors declare that there is no conflict of interest.

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