Neutralization–Reionization Mass Spectrometry (NRMS)

CHRYSOSTOMOS WESDEMIOTIS and FRED W. MCLAFFERTY*

Chemistry Department, Cornell University, Ithaca, New York 14853-1301

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Contents

I. Introduction

Mass spectrometry (MS) has established a reputation for unique applicability for many analytical problems.[1-3] Intuitively, MS is associated with the study of *ions*, originating from a *neutral* molecule, whose identification and/or quantitation is the ultimate goal. In neutralization–reionization mass spectrometry (NRMS) the mass spectrometer is used instead to study *neutral* species. These are produced from mass-selected ions within the mass spectrometer by charge exchange (eq 1) or dissociation (eq 2).[4-23]

$$ABC^+ + M \rightarrow ABC + M^+ \qquad (1)$$

$$ABC \rightarrow AB + C \qquad (1a)$$

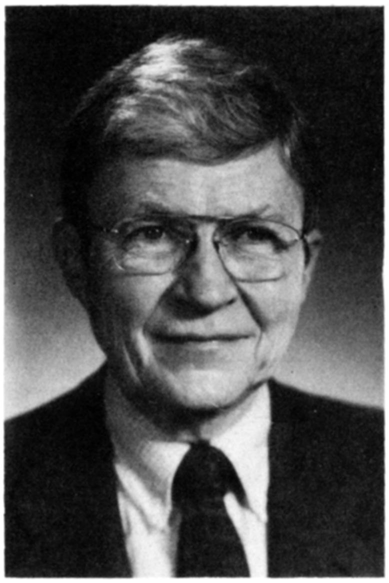
$$ABC^+ \rightarrow AB + C^+ \qquad (2)$$

$$AB \rightarrow A + B \qquad (2a)$$

We will define the route for production of the neutral species in NRMS as the neutralization process. It is achieved by (a) electron transfer as in eq 1,[5,7,9-11,13,15-23] where ABC^+ is any mass-selected ion and M a gaseous target atom; (b) unimolecular or collisionally activated dissociation (CAD) as in eq 2;[4-6,8,9,12-16,20,23] or (c) further dissociation of the primary neutrals resulting from these processes (eq 1a and 2a).[9,15,16,19-22] Similar equations can be written for negative ions, which to date have been infrequently studied. Equation 1 describes the *intermolecular* charge-exchange (CE) neutralization, whereas eq 2 can be viewed as the *intramolecular* dissociative neutralization process. The latter has also been termed "collisionally-induced dissociative ionization";[8] we prefer the designation NRMS for both eq 1 and 2 to retain our original emphasis[4,5] that both focus on the study of neutrals.

Reionization in NRMS, as contrasted to the first ionization in the ion source, is defined as the trans-

Chrysostomos Wesdemiotis was born in 1952 in Thessaloniki, Greece. He received his diploma degree in 1976 and his Ph.D. degree in 1979 from Technical University of Berlin. After performing postdoctoral research with Fred W. McLafferty in 1980 and serving in the Greek Army, he joined Cornell University in 1983 as a Research Associate. His research interests focus on the development of novel mass spectrometry techniques for the study of structures and reactivities in the gas phase.



Fred W. McLafferty received his B.S. (1943; U.S. Army Infantry, 1943–1945) and M.S. degrees from University of Nebraska and his Ph.D. degree from Cornell University and was a postdoctoral fellow at the University of Iowa. At Dow Chemical Co. he was in charge of mass spectrometry and gas chromatography (1950–1956) and was first director of their Eastern Research Laboratory for basic research. He became Professor of Chemistry in 1964 at Purdue University and in 1968 at Cornell. His 300 publications in mass spectrometry and computer applications include six books, three in multiple editions. He is a member of the U.S. National Academy of Sciences and the American Academy of Arts and Sciences.

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formation of the above fast neutral species into ions. This is usually accomplished by collision with gaseous target atoms (although species such as photons or electrons could have specific advantages)[24] and is followed by mass analysis of the resulting ion products. Such mass analysis of both the precursor ions and the reionized neutrals requires tandem mass spectrometry (MS/MS) instrumentation.[3] NRMS with normal MS, without precursor ion separation, could also have analytical utility.[5] We have also proposed neutralization of multiply charged ammonium, oxonium, and other onium ions, producing unstable hypervalent species, as a method for dissociating large ions that have even negligible kinetic energy.[24]

Similar experimental techniques have been used to study electron transfer and energy states of simple oligoatomic species.[25-28] In neutralized ion beam spectroscopy,[29] developed by Porter and co-workers, unstable neutral species such as NH_4 and CH_5 have been generated by neutralization of the corresponding ions and characterized without reionization by the kinetic energy released upon their dissociation.

NRMS *can* provide valuable information on the structures of the prepared neutrals, and their ionic precursors, as well as the original sample molecules. Particularly promising for such structure elucidation is the fact that neutral species often dissociate by different pathways from those of the corresponding ions.[5,19,22] With NRMS, the structure of the *neutral* fragment (AB in eq 2) from an ionic dissociation becomes accessible;[4-6,8,9,12-16,20] previously knowledge of the neutral had to be deduced from thermochemical measurements and/or the structure of the complementary *ionic* fragment (C^+) supplied by collisionally activated dissociation (CAD).[30] Further, the neutralization capability can be used to prepare and investigate hypervalent and other unstable species such as HNC,[5,6] H_2CClH,[5,19] $CH_3C(OH){=}CH_2$,[5] H_2Cl,[21] CH_3OH_2,[5] $^{\bullet}(CH_2)_nOH_2$,[9] and RNH_3[7,9,10,11,29] prepared from the corresponding easily formed ions.

In this paper we have attempted to review the studies since 1980 that deal with formation *and* subsequent reionization of fast (multikilovolt) neutral species in a mass spectrometer. Our focus is on the unique structural information available from NR mass spectra and on the reactivity of the produced neutrals, necessitating incomplete coverage of other important areas such as oligoatomic species and exact energy states of the generated neutrals.

The review first presents a brief explanation of the utilized nomenclature. The experimental part describes optimum methods to obtain NR spectra, including the effect of neutralization and reionization agents. In the application chapters several examples of NR spectra are presented, relating their characteristics to the structures of their ionic or neutral precursors and illustrating the types of unusual neutral species that can be investigated.

II. Nomenclature

We have adopted the following nomenclature to describe the experimental procedure producing the neutralization–reionization mass spectrum (abbreviated NR spectrum). This includes the neutralization and reionization targets as well as the transmittance (*T*, which defines the average number of collisions)[31-34] utilized with these targets. Thus, a Hg (90% *T*)/O_2 (30% *T*) NR spectrum of ABC^+ ions is obtained with Hg charge exchange neutralization (eq 1), elimination of the remaining ions (designated by the slash), and O_2 reionization of the resulting neutrals, the pressures of these targets adjusted so as to give 90% and 30% transmittance of the ions and neutrals, respectively. If the neutrals are produced instead by the unimolecular dissociation of ABC^+ metastable ions (MI) (eq 2, dissociative neutralization), this is called a MI/O_2 (30% *T*) NR spectrum of ABC^+. The spectra produced in these two experiments will represent reference reionization spectra of ABC and AB neutrals, respectively, *only* if these are the only neutrals formed and ionized, which is often difficult to establish with present experimental techniques. Thus we feel that the experimental designation of the spectrum should be based on the known precursor ion, not on its postulated neutral product. Finally, in a Hg (90% *T*)/He (30% *T*)/O_2 (30% *T*) NR spectrum of ABC^+, Hg is used for neutralization and He for CAD of the resulting primary neutrals such as ABC (eq 1a), with the resulting neutral products reionized by O_2; after both of the first two collision processes, any remaining or newly formed ions are deflected. The transmittances may be omitted if the same conditions are used throughout a series of data.

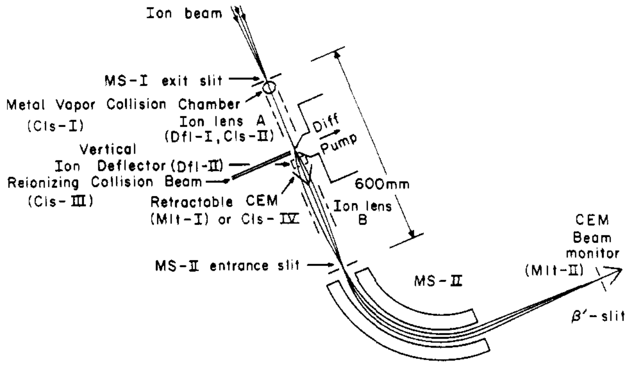


Figure 1. Neutralization–reionization interface: (Cls) collision region; (Dfl) ion deflector; (Mlt) channel electron multiplier.

III. The Experiment and Its Optimization

A. Instrumentation

Neutralization–reionization experiments described to date have been carried out in the field-free regions of tandem mass spectrometers. The original Cornell instrument utilizes a Hitachi RMH-2 double-focusing mass analyzer as MS-I and an electrostatic sector as MS-II;[4,31,32] a final magnetic sector makes possible high-resolution MS-II or MS/MS/MS experiments.[32] Figure 1 shows MS-II and the interface region between MS-I and MS-II incorporating several collision regions and deflectors[15,22,33] (the terminal magnetic sector is not shown). Following the MS-I exit slit there is a metal-vapor furnace or gas inlet for neutralization (collision region I, Cls-I) and an ion lens (lens A) for deflection (Dfl-I) of unneutralized ions. Next an additional collision gas can be introduced separately for dissociation of the primary neutrals (Cls-II).[22] A differentially pumped molecular beam collision region[32] (Cls-III) can also be used for this[22] or for reionization of the neutral species. The use of high pressures here can induce neutral dissociation as well as reionization.[19–22] Cls-III is followed by a second electrostatic ion deflector (Dfl-II) and a retractable channel electron multiplier (Mlt-I) for the direct measurement of neutral abundances. A separate collision device (Cls-IV) can also be used here for reionization.[22] With Mlt-I retracted, ions are mass-analyzed by MS-II and collected with the multiplier (Mlt-II) at the β' focal position to produce the NR mass spectrum.

The metal-vapor collision chamber (Cls-I) can be operated at over 500 °C and is equipped with water-cooled areas to condense efficiently the metal vapor and minimize contamination of the mass spectrometer.[15] With mercury, a special chamber with cryogenic Hg trapping is used and gives significantly lower losses. The Hg trap is cooled with N_2 gas that passes a coil immersed in liquid N_2. The trap temperature can be adjusted as low as −196 °C by regulating the N_2 flow rate; it is usually set between −90 and −150 °C.[35a] For neutralization by gases, the metal-vapor furnace is replaced by a collision chamber with the target gas admitted through a pressure regulator.[15] A similar collision chamber can serve as Cls-II and Cls-IV.[35a] Cls-I, Cls-II, and Cls-IV can easily be removed through vacuum locks.

Because ion signals in NRMS spectra are 3–5 orders of magnitude lower than those in normal mass spectra, a capability for repetitive scanning and averaging of spectra is of high value. The current NRMS data system at Cornell,[31–33] an improved version of one described earlier,[35b] uses a DEC PDP-11/10 minicomputer to effect and collect repeated scans of ESA-II over predetermined mass ranges, displaying each new scan and the summed scans. The precursor ion peak is also displayed on the same spectrum, but in an empty region, by scanning it separately after offsetting the signal designating its ESA voltage (m/z) by an appropriate value. This gives relative cross-section data of high (±<10%) precision, whose utility is discussed below.

The apparatus of Porter et al. contains a magnetic sector as MS-I and an electrostatic deflector as MS-II.[7,10,11] Ions exiting MS-I undergo electron exchange in a heated neutralization chamber with several millitorr of metal vapor. In addition, the neutralization chamber can be floated at a high negative potential in order to increase the kinetic energy of the neutral beam. Unreacted ions are removed by electrostatic deflection, and the remaining neutrals are reionized in a following ionization chamber that can be pressurized with the appropriate collision gas. The reionized beam is deflected off the beam axis. The extent of deflection as measured by the position of a movable detector reflects the energy, and thus the mass, of product ions.

In the twin VG ZAB-2F mass spectrometers of Utrecht (Terlouw et al.) and Ottawa (Holmes et al.) a second collision gas cell is located in front of the existing cell in the second field-free region of the instrument.[13,18] An ion-deflector electrode is placed midway between the two gas cells that host the neutralization and reionization collisions, respectively.[36] The ZAB-2FQ hybrid BEQQ mass spectrometer at the University of Toronto (Harrison et al.) contains two collision cells and an intermediate deflector electrode in the field-free region between the magnetic and electrostatic sectors.[23] The 2AB-HF-3F BEB instrument at the Technical University of Berlin (Schwarz et al.) is similarly equipped in the field free region between the first magnetic and electrostatic analyzers.[17]

In contrast to the original apparatus (Figure 1), only metal-vapor targets have been used so far with Porter's mass spectrometer[7,10,11,29] and only gaseous nonmetallic neutralization targets with the latter three instruments.[6,8,12–14,18,23] For these it should be noted that conventional collision cells[30] could be easily pressurized with Hg because of its relatively high vapor pressure at room temperature. In the NR studies published so far, mass-selected multikilovolt (2–10) primary ion beams have been prepared by either electron or chemical ionization.

B. Neutralization

The optimum target to effect neutralization is one that gives, under the experimental conditions available, a neutral beam of the highest intensity from the precursor ion selected and causes the least scattering losses. The latter is minimized by using the highest ion-accelerating potential of the instrument.[4,15,31] Further, if charge-exchange (CE) neutralization is desired (eq 1), it must be maximized relative to the production of other potentially interfering neutrals formed by CAD (dissociative neutralization, eq 2), and vice versa.

1. Charge Exchange vs. Dissociative Neutralization

For CAD studies helium is usually the target gas of choice because it has the lowest probability for charge exchange;[37,38] the unusually high ionization energy (IE) of helium (24.6 eV)[39] makes it very inefficient as a neutralization target. On the other hand, metal vapors are found particularly appropriate for ion CE neutralization studies.[7,11,15,29]

A thorough investigation by Danis et al. on neutralization cross sections[15,33] reveals that for 10-keV acetone molecular ions the CE:CAD ratio is 0.1 for He, 2.9 for acetone, 3.8 for Xe, 5.9 for Zn, and 7.3 for Hg. Further, the total neutral abundances produced with these five targets, relative to the abundance of the unattentuated acetone$^{\bullet+}$ precursors, are 3.9, 6.5, 7.5, 11, and 16%, respectively. Resonant charge exchange with acetone itself is obviously far from the most efficient charge-exchange neutralization process. Mercury gives the best results and is at the same time particularly convenient because of its high vapor pressure and low reactivity. In further studies, other ions (e.g., $HCO_2CH_3^{\bullet+}$, vide infra) show variable differences in the CE:CAD values for He and Hg; the CE:CAD/Hg for quaternary ammonium ions appears to be unusually low.[9,40] The extent of CE vs. CAD can be determined easily in cases where NR peaks expected from CE reionization differ from those from reionization of CAD neutrals. This will be illustrated for methyl formate ions.[20]

Collisional activation of methyl formate molecular ions with He gives rise to the fragment ions recorded in the CAD spectrum of Figure 2A. The simultaneously produced neutral fragments (eq 2, dissociative neutralization) are observed in the complementary He/O_2 NR spectrum (Figure 2B) whose $CO^{\bullet+}$ base peak corresponds to the $CH_3OH^{\bullet+}$ (CO loss) base peak of the

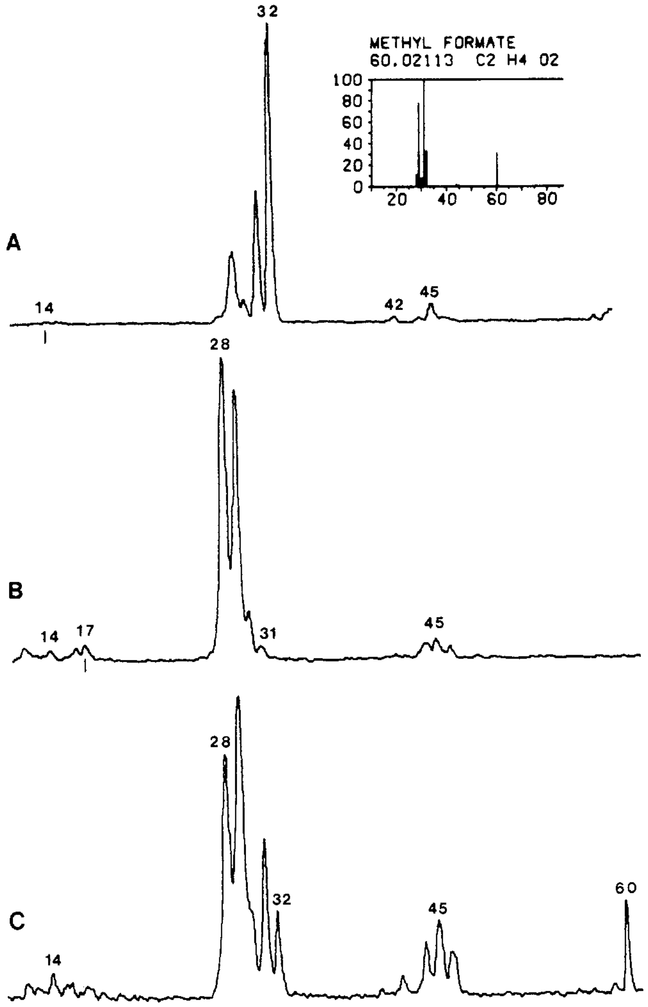


Figure 2. (A) CAD/He spectrum of $HCO_2CH_3{}^{\bullet+}$. (Inset) EI spectrum of methyl formate. (B) He/O_2 and (C) Hg/O_2 NR spectra of $HCO_2CH_3{}^{\bullet+}$.

CAD spectrum. Similarly, the *m/z* 29, 31, and 32 peaks of Figure 2B correspond to the reionized neutrals formed with *m/z* 31, 29, and 28 ions of Figure 2A.

The absence of the reionized precursor (*m/z* 60) in the He/O_2 NR spectrum indicates that interaction of methyl formate ions with He causes almost exclusively CAD. Alternatively, the superiority of Hg for charge exchange (CE) is documented in the Hg/O_2 NR spectrum of $HCO_2CH_3{}^{\bullet+}$ (Figure 2C), which contains several ions (*m/z* 60, 32, and 31) expected from reionization (and dissociation) of HCO_2CH_3 according to its EI spectrum.[41] However, the concomitant appearance of intense $CO^{\bullet+}$ (*m/z* 28) in the Hg/O_2 NR spectrum indicates that CAD also takes place with Hg (the abundance of *m/z* 28 is only 10% in the EI spectrum). The absolute abundance of $CO^{\bullet+}$ (from the same amount of neutrals) is ~2 times larger in the He/O_2 NR spectrum, showing that collision of $HCO_2CH_3{}^{\bullet+}$ with mercury targets produces approximately equal amounts of neutrals by CE and CAD.

In the Xe/He NR spectrum of $HCO_2CH_3{}^{\bullet+}$,[18] *m/z* 28 becomes the base peak and [*m/z* 60]:[*m/z* 28] = 0.015 vs. 0.38 in the Hg/O_2 NR spectrum of Figure 2C.[20] The smaller ratio for the Xe/He combination is partly due to the higher fragmentation extent with He reionization (vide infra)[16] but mainly reflects the substantially better CE:CAD ratio for Hg than for Xe neutralization targets.[15]

2. Target Gas Pressure

As recommended for CAD studies,[30a] the maximum abundance of neutral products can be produced by increasing the neutralization target pressure until the precursor ion flux has been reduced to ~30% of its initial value.[15] At these transmittances multiple collisions[34] cause increased fragmentation (eq 1a and 2a) that can be valuable for structural characterization of the neutral and/or its precursor ion (vide infra).[22] However, if maximum purity of the primary neutralization product (eq 1 and 2) is desired, single-collision conditions[34] should be used to avoid secondary dissociations (e.g., 90% and 70% transmittances yield 1.06 and 1.2 scattering collisions, respectively, on average for affected ions).[15,34] To illustrate this possible pitfall, we found the MI/O_2 (50% *T*) and CAD/O_2 (50% *T*) NR spectra of $CH_3COOCH_3{}^{\bullet+}$ to be closely similar, from which we concluded that the $^{\bullet}CH_2OH$:$CH_3O^{\bullet}$ isomeric composition of the C, H_3, O neutrals produced under these different conditions was closely similar.[20] However, as discussed further below, Holmes found (and we have confirmed) significant differences in these spectra measured at 80% transmittance.[36b]

3. Internal Energies of Neutrals Formed by CE

Targets of much lower ionization energy (IE)[39] than the neutral formed from the ion will produce neutrals of higher average internal energy.[15,29] Neutralization of $CH_3COCH_3{}^{\bullet+}$ with a target of much lower IE value (4.6 eV lower for Na)[39] than that of acetone leads to the formation of acetone neutrals in excited states (Figure 3B); the greater abundances of *m/z* 43, 42, and 28 in the Na/O_2 NR spectrum compared to those in the Hg/O_2 NR spectrum (Figure 3A) are consistent with dissociations of the newly formed CH_3COCH_3 to $CH_3CO^{\bullet}$ and CH_2CO and the further dissociation of $CH_3CO^{\bullet}$ (Figure 3C) to CO.

On the other hand, neutrals of relatively low internal energy appear to be produced by neutralization targets of the same or higher IE as that of the neutralized precursor. T/O_2 NR spectra of acetone$^{\bullet+}$ using as neutralization targets (T) O_2, CH_3COCH_3, Xe, and Zn were all closely similar to that of Hg shown in Figure 3A.[15] However, severe Franck–Condon factors accompanying the vertical neutralization process can also form excited neutrals. Examples will be given in Applications.[20]

4. Collection Efficiency in NR Spectra

By far the most favorable CAD process for $CH_3COCH_3{}^{\bullet+}$ yields $CH_3CO^+ + CH_3{}^{\bullet}$.[42] Consequently, $CH_3{}^{\bullet}$ should be the most abundant neutral from CAD. However, in the corresponding NR spectrum (actually the first NR spectrum measured at Cornell),[4b] even with He neutralization targets (~90% CAD, vide infra), the abundance of $CH_3{}^+$ (*m/z* 15) is less than that of *m/z* 43.[4b,15,31,33] The dissociative neutralization process $CH_3COCH_3{}^{\bullet+} \rightarrow CH_3{}^{\bullet} + CH_3CO^+$ is accompanied by a high (0.11 eV) translational energy release at threshold,[39a] so the low *m/z* 15 abundance must be due to the combined poor efficiencies of transmitting $CH_3{}^{\bullet}$ (as postulated originally)[4b] and $CH_3{}^+$ and probably of reionizing $CH_3{}^{\bullet}$ (vide infra).

This postulated effect of acceptance angle and ion pathlength on the relative abundances in a NR spec-

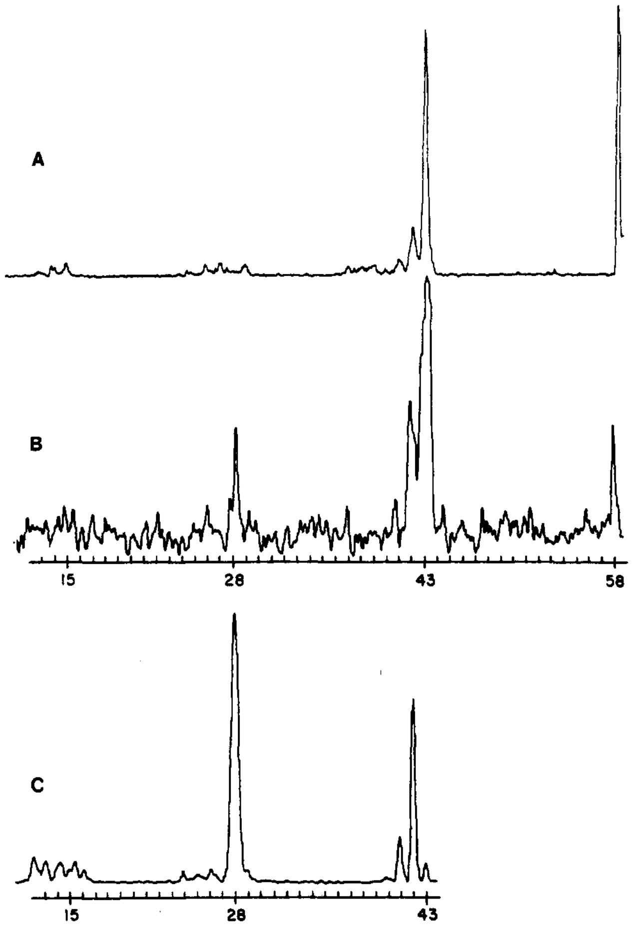


Figure 3. (A) Hg/O_2 and (B) Na/O_2 NR spectra of $CH_3COCH_3^{\bullet +}$ ions from acetone and (C) Hg/O_2 NR spectrum of CH_3CO^+ ions from acetone. The high noise level of the middle spectrum is substantially reduced by lowering the Na pressure.

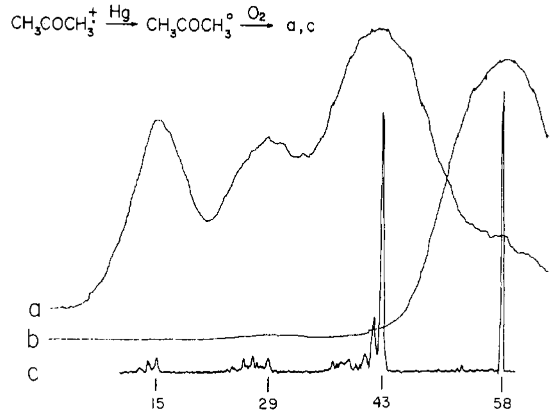


Figure 4. Hg/O_2 NR spectra of $CH_3COCH_3^{\bullet +}$ collected at (a) Mlt-I, and (c) Mlt-II (see Figure 1). (b) MS-II mass spectrum collected at Mlt-I of m/z 58 ions from MS-I.

trum is dramatically supported by Figure 4, recorded with the Figure 1 instrument.[15,33] The minimal resolution Hg/O_2 NR spectrum of $CH_3COCH_3^{\bullet +}$ in Figure 4A was obtained at the retractable multiplier Mlt-I by using the ion deflector Dfl-II for mass separation, while spectrum 4B is the calibration for spectrum 4A showing the exact position of m/z 58; the conventional NR spectrum detected at Mlt-II after mass separation through MS-II is illustrated in Figure 4C. The reionized precursor, m/z 58, is obviously produced with a much narrower angular distribution since from spectrum 4A to 4C there is more than an order of magnitude increase in its relative abundance. The abundances of m/z 29 and 15 relative to that of m/z 43 decrease severely from spectrum 4A to 4C, indicating that the production of m/z 29 and 15 occurs with much larger divergence than that of m/z 43. Thus, in the use of NRMS to identify neutral products of small fractional mass formed with a substantial release of translational energy, low abundances do not necessarily mean that formation of the corresponding neutral is unfavorable.[9,19]

C. Reionization

Reionization to produce positive ions is accomplished by collision of the fast neutral beam (projectile) with gaseous targets (our preliminary findings on producing negative ions are mentioned later). The abundance of the resulting ionic products relative to that of the precursor neutral is the reionization efficiency of the respective neutral species.[16]

For the hypervalent neutrals He_2, H_3, ND_4, and N_2D_7 of very low (<4.7 eV) IE values studied by Gellene and Porter, NO_2 was found to be the most efficient reionization target.[10] This could be due to the near resonance between the electron affinity[43] of NO_2 (2.3 eV) and the IE values of the neutrals. For fast neutrals of higher IE value, the electron affinity plays a much less significant role in reionization efficiency as is shown for fast Ar atoms[44] and CH_3COCH_3 or CH_3Cl molecules.[16,33]

Reionization efficiencies depend on both the projectile and the target. A detailed study by Danis et al.[16,33] involving CH_3COCH_3, CH_3Cl, and $^{\bullet}CH_2NH_2$ projectiles and O_2, NO, Cl_2, NO_2, N_2, He, CH_4, SF_6, and Xe targets finds that O_2 is generally the optimum target. The individual values of the O_2 reionization efficiencies show, however, significant differences, with values of 0.24%, 0.45%, and 0.46% for CH_3COCH_3, CH_3Cl, and $^{\bullet}CH_2NH_2$, respectively, using the instrument shown in Figure 1 and with ion collection at Mlt-II.[16] For fast acetone molecules produced from $CH_3COCH_3^{\bullet +}$ with Hg, the reionization efficiencies relative to that with O_2 targets (1.0) are 0.43, 0.42, 0.29, 0.07, and 0.09 for NO_2, N_2, He, SF_6, and Xe, respectively.[16] Parallel trends are observed for other fast neutral species.[16,33] The data are generally similar to target efficiencies found for charge stripping.[45–47]

Electron removal from a fast neutral ($\bar{M}$, upper bar denotes fast species) upon collision with a target (A) can occur by electron detachment (eq 3) or by inverse neutralization (eq 4). A "reverse" experiment[48] using

$$\bar{M} + A \rightarrow \bar{M}^+ + e^- + A \qquad (3)$$

$$\bar{M} + A \rightarrow \bar{M}^+ + A^- \qquad (4)$$

fast O_2 and N_2 produced by Hg neutralization of $O_2^{\bullet +}$ and $N_2^{\bullet +}$, respectively, and CH_3Cl and CH_3COCH_3 targets shows that O_2 forms O_2^- and O^-, while no N_2^- or N^- is observed.[16] Thus, the capability for effecting inverse neutralization appears to be an important factor in the superiority of O_2 as a reionization target for fast neutrals of higher IE values.

Changes from 3 to 10 keV in the kinetic energy of CH_3Cl, $^{\bullet}CH_2NH_2$, $^{\bullet}S$, and $^{\bullet}CH_3$ neutrals affect their reionization efficiency by less than a factor of 2.[16,33] This is encouraging, as the reionization efficiencies of neutral fragments from ion decompositions (eq 2), which will have a fraction of the initial ion kinetic en-

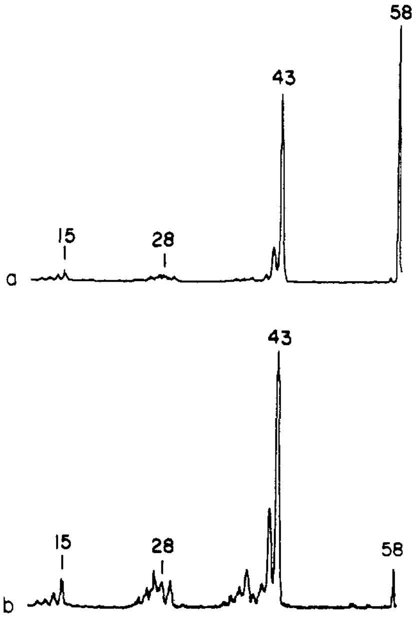


Figure 5. NR mass spectra of CH_3COCH_3 with reionization at 30% transmittance by (a) O_2 and (b) He.

ergy, will not be affected greatly by mass. However, for the overall neutralization–reionization experiment, the highest kinetic energy possible is recommended to minimize scattering losses and increase transmittance (vide supra).[15]

1. Effect of Target on Extent of Dissociation upon Reionization

Fragment ions in the NR spectrum result from dissociation both upon neutralization (which is minimized by using Hg, Figure 3)[15] and upon reionization. Reionization of fast CH_3COCH_3 molecules with O_2, NO, Cl_2, NO_2, N_2, He, CH_4, SF_6, and Xe yields $CH_3COCH_3^{\bullet+}$ and fragment ions, with [$CH_3COCH_3^{\bullet+}$] being 41, 19, 25, 18, 11, 3.7, 2.7, 2.5, and 1.5% of the total abundance of reionized species, respectively.[16,33] Evidently, the targets fall in mainly two classes: O_2, NO, Cl_2, and NO_2 are "soft" reionizing agents providing a smaller degree of fragmentation than do the "hard" agents He, CH_4, SF_6, and Xe, while N_2 occupies an intermediate position. In general, the soft targets are also those capable of accepting an electron in the reionization process (eq 4), a reaction that should have a lower energy requirement than eq 3 and produce reionized species of lower average internal energy.[44] To illustrate, in the NR spectra of $CH_3COCH_3^{\bullet+}$ (Figure 5) the increase in fragmentation is dramatic upon changing the reionizing target from O_2 to He.

2. Choice of Target and Pressure

The type of information and degree of sensitivity needed should be considered in selecting the target and pressure for reionization in NRMS. For structural information a large extent of fragmentation can be desirable. This can be accomplished with He reionization (Figure 5) and/or by an increase in the pressure to produce multiple collisions[34] causing CAD of the neutrals and ions (vide infra).[16,19,21,22]

For "molecular weight" information, as in the case where a mixture of neutrals is produced and identity of each is desired, minimum fragmentation is necessary. Thus, O_2 is the preferred target, used at the lowest pressure, giving sufficient sensitivity to avoid secondary dissociative collisions.[16] Because reionization efficiencies vary substantially between species (vide supra), the interpretation of spectra due to more than one neutral species requires that the relative efficiency of reionizing each neutral must be determined.[20]

D. Collisionally Activated Dissociation of Neutrals

NRMS can provide unique molecular information from the dissociation of neutrals, as these reactions are often different from those of their ionic counterparts, involving less prior rearrangement. For such dissociations, energetically excited neutrals can be produced by vertical neutralization (eq 1) with a metal vapor of low ionization energy (Figure 3B)[15,33] or by an ionic dissociation (eq 2) that has a significant amount of reverse activation energy.[49] These neutrals can dissociate further unimolecularly (eq 1a and 2a, respectively) if their internal energies lie above the respective dissociation thresholds. Alternatively, neutral species with insufficient internal energy, such as those formed by Hg neutralization,[15] can be caused to dissociate prior to reionization by collisional activation. As a first method for this, a higher pressure of the reionization gas can cause neutral dissociation in a first collision and product reionization in the second. The dissociation and ionization energies of organic molecules vary between 3–5 and 7–11 eV,[39] respectively, so that the relative cross sections for dissociation are generally higher than those of reionization. By use of the instrumentation illustrated in Figure 1,[15] collisionally activated dissociation (CAD)[30] of the primary neutrals formed at Cls-I has been achieved by raising the reionization target pressure at the reionization region (Cls-III).[16,19,21,33] A separate collision region gives added flexibility; with the Figure 1 instrument and neutralization in Cls-I, neutral dissociation and reionization have been successfully carried out in Cls-II and -III, respectively, and also in Cls-III and -IV.[22]

CAD of the neutrals provides valuable information on the structures of both the neutrals and their ionic precursors.[5,9,16,19,21] The significance of such structural elucidation lies in the fact that neutral species often dissociate by different pathways from those of the corresponding ions, e.g., the weakest bond in $H_3CCl^{\bullet+}$ is H–C, while that in neutral H_3CCl is C–Cl.[39,50–52] This is documented in the NR spectra of parts A and B of Figure 6, respectively;[19] in the Hg/He NR spectrum of $H_3C^{37}Cl^{\bullet+}$ obtained under single-collision reionization conditions (Figure 6A), the fragment ion abundances resemble closely those of the CAD spectrum of $H_3C^{37}Cl^{\bullet+}$ [19,33,53] and the EI spectrum of H_3CCl.[41] Thus most ions of Figure 6A result from dissociation of $H_3CCl^{\bullet+}$ upon reionization, with $H_3CCl^{\bullet+} \rightarrow H^{\bullet} + H_2CCl^+$ as the dominant fragmentation channel. Increasing the He pressure to lower transmittance (Figure 6B) causes multiple collisions and a dramatic increase in [Cl^+] via $H_3CCl \rightarrow H_3C^{\bullet} + Cl^{\bullet}$. The low abundance of CH_3^+ is probably due to the low collection efficiency for smaller dissociation products (vide supra).[4,15,31]

CAD has been used successfully to determine ionic structures.[30] As shown above, it can also be used to identify structural elements of neutral molecules.

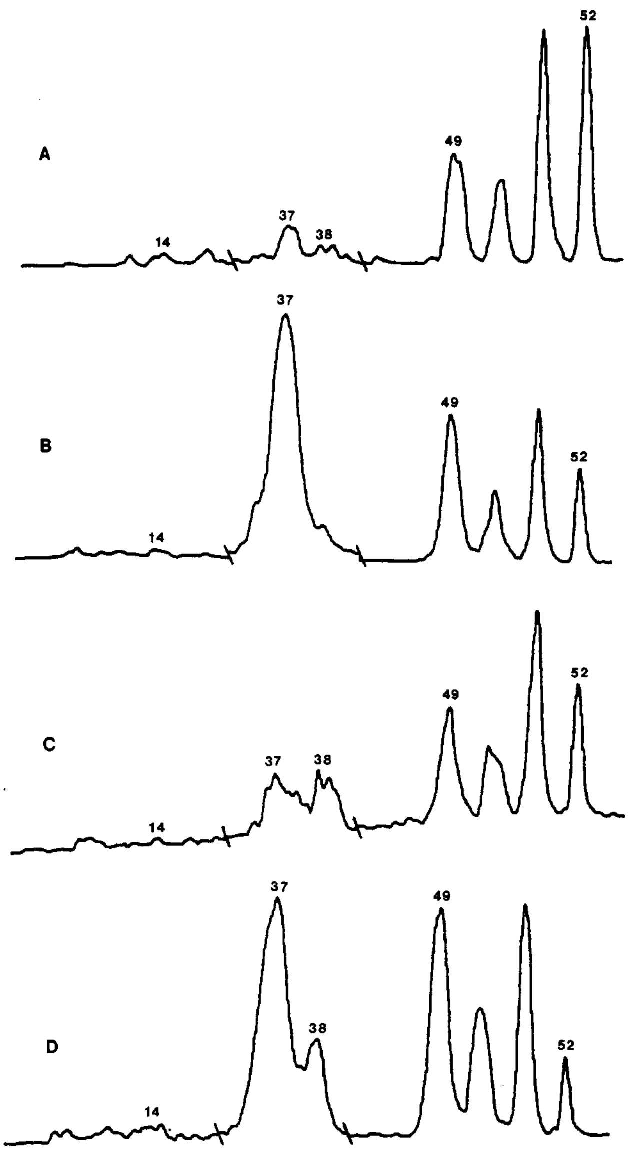


Figure 6. Hg/He NR spectra of $H_3C^{37}Cl^{\bullet+}$ (A, B) and $H_2C^{37}ClH^{\bullet+}$ (C, D) at transmittances with He of 90% (A, C) and 30% (B, D).

Particularly valuable for such characterizations is the fact that neutrals generally show a much smaller tendency for isomerizations than do ions. The major dissociation of distonic ${}^{\bullet}CH_2CH_2CH_2NH_3^+$ ions involves H rearrangements followed by $C_2H_5^{\bullet}$ loss, while the corresponding $CH_2CH_2CH_2NH_3$ neutrals dissociate directly via NH_3 elimination.[9] Similarly, 1- and 2-butene cations are separated by such a low isomerization barrier that they interconvert before dissociation under both EI[41] and CAD[30] conditions. This equilibration is frozen upon neutralization, and the Hg/He/NO NR spectra of 1- and 2-butene ions are significantly different; CAD/He of the neutral molecules follows different channels for $CH_2{=}CHCH_2CH_3$ and $CH_3CH{=}CHCH_3$, with the allylic cleavages being now the dominant fragmentation pathway.[22]

IV. Applications

A. Structure of Neutrals from Ion Dissociations

The gas-phase unimolecular dissociation of an organic ion produces a fragment ion and a neutral (eq 2). The conventional mass spectroscopic techniques of metastable ion (MI)[49,54] and collisionally activated[30,55,56] dissociations measure the ionic products of these reactions only. However, the structure of the neutral product is equally important for the postulation of a dissociation mechanism. With NRMS direct measurement of the neutral dissociation product structure becomes possible.

1. CHN from Metastable $C_6H_5NH_2^+$ Ions

Metastable aniline molecular ions undergo dissociation principally to $C_5H_6^{\bullet+}$ and CHN (eq 5). On the

$$C_6H_5NH_2^{\bullet+} \rightarrow C_5H_6^{\bullet+} + CHN \tag{5}$$

basis of the expected stability of HCN over HNC it was concluded that electron impact on aniline produces $C_5H_6^+$ + HCN.[57-59] A more recent thermochemical investigation by Lifshitz et al.[60] proposed, however, that the threshold dissociation of aniline ions proceeds via elimination of the less stable[61] HNC molecule.

The MI/He (50% *T*) NR spectrum of $C_6H_5NH_2^{\bullet+}$ obtained with the instrument of Figure 1 by He reionization of the CHN neutral from eq 5 shows [*m/z* 26]:[*m/z* 27] = 0.8, compared to ratios of 1.5 and 0.8 in the Hg/He (50% *T*) reference NR spectrum of $HCN^{\bullet+}$ and $HNC^{\bullet+}$ (from H_3CNH_2),[62] respectively.[5,33] Thus, the metastable aniline ion dissociates via HNC, not HCN, elimination in agreement with the postulate of Lifshitz. Independent work by Holmes et al.[6a] reached the same conclusion based on the interpretation of the *m/z* 12–15 region in the MI/He NR spectra of ionized aniline and pyridine. The unimolecular fragmentation of the latter is known to yield HCN neutrals together with $C_4H_4^{\bullet+}$ ions,[63,64] as confirmed by NRMS.[5,33] Metastable benzonitrile cations also lose HCN; the [*m/z* 26]:[*m/z* 27] ratio from reionization of HCN (from $C_6H_5CN^{\bullet+}$) and HNC (from $C_6H_5NH_2^{\bullet+}$) measured by Holmes et al. with the modified ZAB-2F under single-collision He reionization (≥80% transmittance of the neutral beams) is 0.24 and 0.13, respectively.[6b] Different abundance ratios are observed now because of the different transmittances utilized. At 50% transmittance (above) some CAD of the neutral CHN molecules prior to reionization increases the CN^+ intensity observed at *m/z* 26.

2. COH_3 from Metastable $CH_3CO_2CH_3^{\bullet+}$ Ions

The unimolecular dissociation of metastable methyl acetate radical ions proceeds almost exclusively by loss of COH_3 and formation of acetyl ions (eq 6).[65-67] Al-

$$CH_3COOCH_3^{\bullet+} \rightarrow CH_3CO^+ + COH_3^{\bullet} \tag{6}$$

$$CH_3CH_2COOCH_3^{\bullet+} \rightarrow CH_3CH_2CO^+ + CH_3O^{\bullet} \tag{7}$$

though initial studies suggested that the neutral fragment lost is the methoxy radical,[65-68] recent investigations by Burgers et al.[8,12,69] report that the $COH_3^{\bullet}$ neutral formed with CH_3CO^+ is mainly (92%) ${}^{\bullet}CH_2OH$, not $CH_3O^{\bullet}$, as its He reionization spectrum (1) matches better the CAD spectrum of CH_2OH^+ cations than the charge reversal spectrum of CH_3O^- anions[70] and (2) is different from the reionization spectrum of $COH_3^{\bullet}$ neutrals from metastable methyl propanoate ions whose unimolecular fragmentation to $CH_3CH_2CO^+$ involves $CH_3O^{\bullet}$ elimination (eq 7). These conclusions assumed identical reionization cross sections for these radicals[69] and were based on the abundances of the small ions of

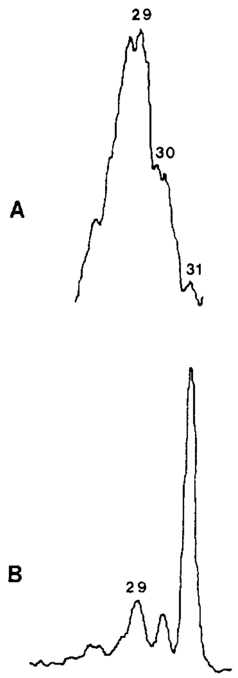


Figure 7. Partial MI/O_2 (50% *T*) NR spectra of (A) $(CH_3O)_2CHN(CH_3)_2^{\bullet+}$ and (B) $HOCH_2CH_2N(CH_3)_2^{\bullet+}$.

m/*z* 15 and 17, characteristic of $CH_3O^{\bullet}$ and $^{\bullet}CH_2OH$, respectively. We have used the *m*/*z* 28–31 regions to differentiate these radicals;[20] comparison to reference NR spectra of $CH_3O^{\bullet}$ and $^{\bullet}CH_2OH$ (Figure 7) from eq 8 and 9, respectively, shows that the great majority

$$(CH_3)_2NCH(OCH_3)_2^{\bullet+} \rightarrow (CH_3)_2NCHOCH_3^{+} + {}^{\bullet}OCH_3 \quad (8)$$

$$(CH_3)_2NCH_2CH_2OH^{\bullet+} \rightarrow (CH_3)_2NCH_2^{+} + {}^{\bullet}CH_2OH \quad (9)$$

(>90%)[71] of COH_3 radicals formed in the CAD unimolecular dissociation of methyl acetate cations (eq 6) have the $CH_3O^{\bullet}$, not the $^{\bullet}CH_2OH$, structure. This is based on our observation that the O_2 reionization efficiency for $CH_3O^{\bullet}$ is only ~25% of that for $^{\bullet}CH_2OH$ at the same kinetic energy;[20] Holmes and co-workers have recently confirmed these conclusions.[36b] Harrison[23a] also reports similar MI/He NR spectra of $CH_3CH_2CO_2CH_3^{\bullet+}$ and $CH_3CO_2CH_3^{\bullet+}$ recorded with a BEQQ instrument.

For the dissociation of metastable $CH_3CO_2CH_3^{\bullet+}$ ions we find[20,71] these neutrals to be 70–80% $CH_3O^{\bullet}$ (and the balance $^{\bullet}CH_2OH$), while the more recent studies of Holmes[36b] report 73% (±5%), in good agreement. We have suggested that the $CH_3O^{\bullet}$ initially formed may be even higher because part undergoes isomerization to the more stable[52,72] $^{\bullet}CH_2OH$ in the nearly 1 μs before reionization.[20] This point is still under investigation; Holmes gives arguments against this,[36b] while Harrison cites evidence for this.[23b] Low-energy formation of $^{\bullet}CH_2OH$ from $CH_3CO_2CH_3^{\bullet+}$ is supported by sophisticated ab initio calculations[72b] proposing that *threshold* dissociation involves isomerization to the distonic radical ion $CH_3C(=OH^{+})OCH_2^{\bullet}$, which further rearranges to the ion–dipole complex $CH_3CO\cdots H\cdots OCH_2^{\bullet+}$; the latter, presumably from its first excited electronic state,[72b] produces CH_3CO^{+} + $^{\bullet}CH_2OH$. Our current studies utilize reionization to negative ions, for which $CH_3O^{\bullet}$ has a much higher cross section than $^{\bullet}CH_2OH$.[22]

3. Other Neutrals from Ionic Fragmentations

Various common neutral species have been characterized in this way. The first NRMS experiment involving a polyatomic organic precursor reported the generation of $CH_3^{\bullet}$ from metastable or collisionally activated acetone ions.[4b,31] The collection efficiency of $CH_3^{\bullet}$ from $CH_3COCH_3^{\bullet+}$ is very small (vide supra);[15] $CH_3^{\bullet}$ neutrals can be generated with a much better yield via CAD of $CH_3CH_2NH_2^{\bullet+}$ ions.[20] As expected,[16] He reionization of $CH_3^{\bullet}$ [12] leads to significantly more fragmentation than O_2 reionization does.

Ethyl and vinyl radicals have been formed by CAD of $CH_3CH_2CH_2OH^{\bullet+}$ [8] or $CH_3CH_2CH_2NH_2^{\bullet+}$ (vide infra)[20] and $^{\bullet}CH_2CH_2NH_3^{+}$ ions,[9] respectively, allyl radicals via unimolecular dissociation from ionized isobutyl alcohol,[8] and formyl[14] and acetyl[12] radicals by unimolecular dissociation of $CH_3COCH_2OH^{\bullet+}$ and $CH_3COCOCH_3^{\bullet+}$, respectively. Upon reionization they all produce spectra that are characteristic of their structures.

Molecules generated by dissociative neutralization for NRMS study include H_2O (from $CH_3CH_2CH_2OH^{\bullet+}$),[8] C_2H_2 (from $C_6H_5CH_3^{\bullet+}$),[12] C_2H_4 (from $C_3H_7O^{+}$, formed from diethyl ether),[12] CH_3OH (from $C_4H_7O_2^{+}$, generated from methyl butyrate or isobutyrate),[12] C_2H_6 (from $CH_3CH_2COCH_2CH_3^{\bullet+}$),[12] and C_6H_6, CH_3CO_2H, and HCO_2CH_3 (from the respective proton-bound dimers).[18] Schwarz et al. showed recently that the $C_2H_4O_2$ molecule cogenerated with $C_4H_8^{\bullet+}$ from metastable *n*-hexanoic acid and *n*-butyl acetate ions is CH_3CO_2H and not its enol.[73] In all cases reionization with O_2 is both the most efficient in terms of absolute product ion abundances and leads to the least fragmentation (highest abundance of undissociated reionized precursor).[16]

B. Generation and Characterization of Unconventional Neutral Species

The stability order of isomers can be changed dramatically by adding or removing an electron.[73] For example, neutral methanol (CH_3OH) is more stable than its CH_2OH_2 ylide isomer,[75,76] but the reverse is true for the respective monocations.[77] Many positive ions, such as NH_4^{+}, H_2Cl^{+}, $CH_2ClH^{\bullet+}$, and $CH_2CH_2NH_3^{\bullet+}$, with significant barriers toward dissociation or isomerization[78] have only marginally stable neutral counterparts that cannot freely exist in condensed phases, so that theory has previously been the most definitive means for their study. The neutralization capability of NRMS offers here a novel route to prepare hypervalent or unstable species in the gas phase from the corresponding easily accessible ions. NRMS thus complements molecular orbital theory by providing experimental data for comparison.

1. Enols

One of the first organic molecules generated via charge-exchange neutralization was the enol of acetone,[5,33] which in solution readily isomerizes to the keto form.[79] The ionized enolic form is a very common rearrangement fragment in the mass spectra of methyl ketones[1] and is both thermodynamically and kinetically more stable than ionized acetone itself.[80] The NR spectra of the acetone enol ion and its isomeric acetone molecular ion have been obtained with several neutralization and reionization agents.[5,13,15,16,23,33] In all cases the abundance of the reionized undissociated precursor at m/z 58 ($C_3H_6O^{\cdot+}$) is larger for the enol; this is consistent with the relative stability of the molecular ions,[80] not their neutrals,[81] indicating that most of the fragmentation occurs after reionization. The appearance of an intense m/z 31 peak in the spectrum of the enol is characteristic for an alcohol functionality,[1] consistent with the enolic structure.

The prototype enol, vinyl alcohol ($CH_2{=}CHOH$), and its tautomer, hydroxymethylcarbene (CH_3COH), which are also inaccessible in pure form in condensed phases, have been prepared by Hg neutralization from the corresponding stable radical cations[82] and both found to survive neutralization, yielding upon He reionization spectra that are different from that of acetaldehyde ($CH_3CH{=}O$),[83] the global C_2H_4O energy minimum.[84] CAD of neutral vinyl alcohol proceeds in part via $CH_2{=}CHOH \rightarrow CH_3COH \rightarrow CH_3CO^{\cdot} + {}^{\cdot}H$; the energy of the transition state of the rate-determining 1,2 H-migration lies ~80 kcal/mol above that for $CH_2{=}CHOH$ and ~30 kcal/mol above that for CH_3COH.[83] The symmetry-allowed antarafacial 1,3 H-rearrangement $CH_2{=}CHOH \rightarrow CH_3CH{=}O$ is not observed.[84] Hydroxymethylcarbene molecules[85] from $CH_3COH^{\cdot+}$ neutralization equilibrate partly with $CH_3CH{=}O$ but not with $CH_2{=}CHOH$, indicating a lower energy barrier for their isomerization to $CH_3CH{=}O$ than to $CH_2{=}CHOH$, setting thus at ~80 kcal/mol the required activation energy for the overall enol to keto tautomerization $CH_2{=}CHOH \rightarrow CH_3COH \rightarrow CH_3CH{=}O$.

2. Ylides

Theoretical and experimental studies show that simple ylide ions are usually equally or more stable thermodynamically than their conventional isomers, separated from them by high isomerization barriers.[53,78] On the other hand, stable ylides are so rare[86] that most characterizations of the prototype ylides H_2CYH (Y = Cl, F, OH, and NH_2) have been based on molecular orbital theory.[75,76,87-90] In the gas phase, fast neutral ylides have been prepared from the corresponding ylide ions (eq 10) and characterized by CAD and reionization.[5,13,19,33]

$$^{\cdot}CH_2YH^+ \xrightarrow[(Hg)]{+e^-} CH_2YH \qquad Y = Cl, F, OH, NH_2 \tag{10}$$

The Hg/He NR spectra of $CH_2ClH^{\cdot+}$ are shown in Figure 6 along with the spectra of its conventional $CH_3Cl^{\cdot+}$ isomer. The appearance of reionized molecules (m/z 52, for $C^{37}ClH_3^{\cdot+}$) in parts C and D of Figure 6 proves that some of the $CClH_3$ neutrals formed upon charge exchange with Hg from $CH_2ClH^{\cdot+}$ survived neutralization (~1 μs). Collisionally activated dissociation of these neutrals prior to reionization, accomplished by raising the He pressure from 90% (Figure 6C) to 30% (Figure 6D) transmittance, increases the abundance of $HCl^{\cdot+}$ (m/z 38) relative to that of $CClH_3^{\cdot+}$ by a factor of 3. This HCl must come from unisomerized CH_2ClH molecules, as CH_3Cl yields $Cl^{\cdot}$ (Figure 6A,B), not HCl upon CAD, in line with its conventional structure. A quantitative analysis of the CAD data of Figure 6 and the charge stripping[47] data of Figure 8 reveals that less than half of the CH_2ClH molecules formed by vertical neutralization dissociate after 10^{-6} s, and of these more than half retain their CH_2ClH ylide structure.[19]

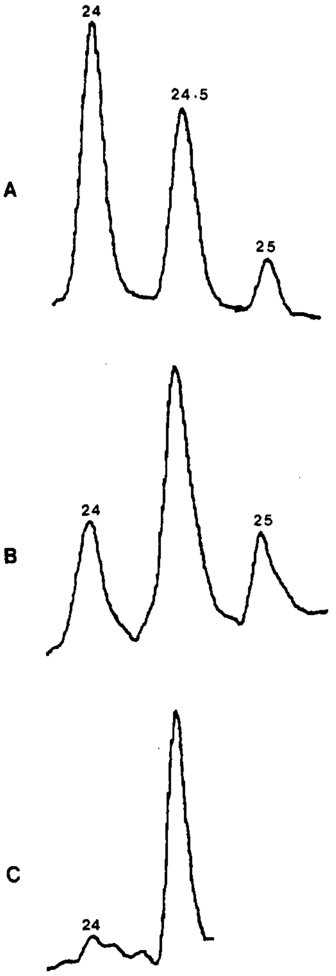


Figure 8. Charge stripping region of Hg/O_2 (30% T) NR spectra of (A) $CH_3{}^{35}Cl^{\cdot+}$, (B) $CH_2{}^{35}ClH^{\cdot+}$, and (C) $CH_2{}^{35}Cl^+$. Peak heights of m/z 24.5 relative to those of the reionized precursor are (A) 0.025%, (B) 0.11%, and (C) 0.29%. The ^{35}Cl isotopomers are used for increased sensitivity. The NR spectra of the ^{35}Cl and ^{37}Cl isotopomers are identical within experimental error.

Similarly, CH_2FH, CH_2OH_2, and CH_2NH_3 have been prepared from their fast gaseous $CH_2YH^{\cdot+}$ ions by Hg neutralization.[19] Reionization of the resulting fast neutrals produces abundant molecular ions in all cases. CAD of these neutrals increases the relative abundance of YH dissociation products, which must originate from CH_2YH, not CH_3Y, indicating that an appreciable fraction of each of these ylides must have survived for the microsecond lifetime of the experiment. The experimental detectability of the four ylides studied requires that they all represent local minima in the respective potential energy surfaces with finite barriers toward dissociation and isomerization, in contrast to theoretical predictions that only CH_2NH_3 is an equilibrium structure.[75,90] This discrepancy could be due to the fact that the experimentally detected neutrals are metastable excited states of the ylides.[91]

3. Zwitterion Neutrals

The Hg/O_2 NR mass spectra of the distonic[78] radical ions $^{\cdot}CH_2CH_2OH_2{}^+$ and $^{\cdot}CH_2CH_2NH_3{}^+$ (parts B and D of Figure 9) bear undissociated precursor ions at m/z 46 ($C_2H_6O^{\cdot+}$) and 45 ($C_2H_7N^{\cdot+}$), respectively.[9] These

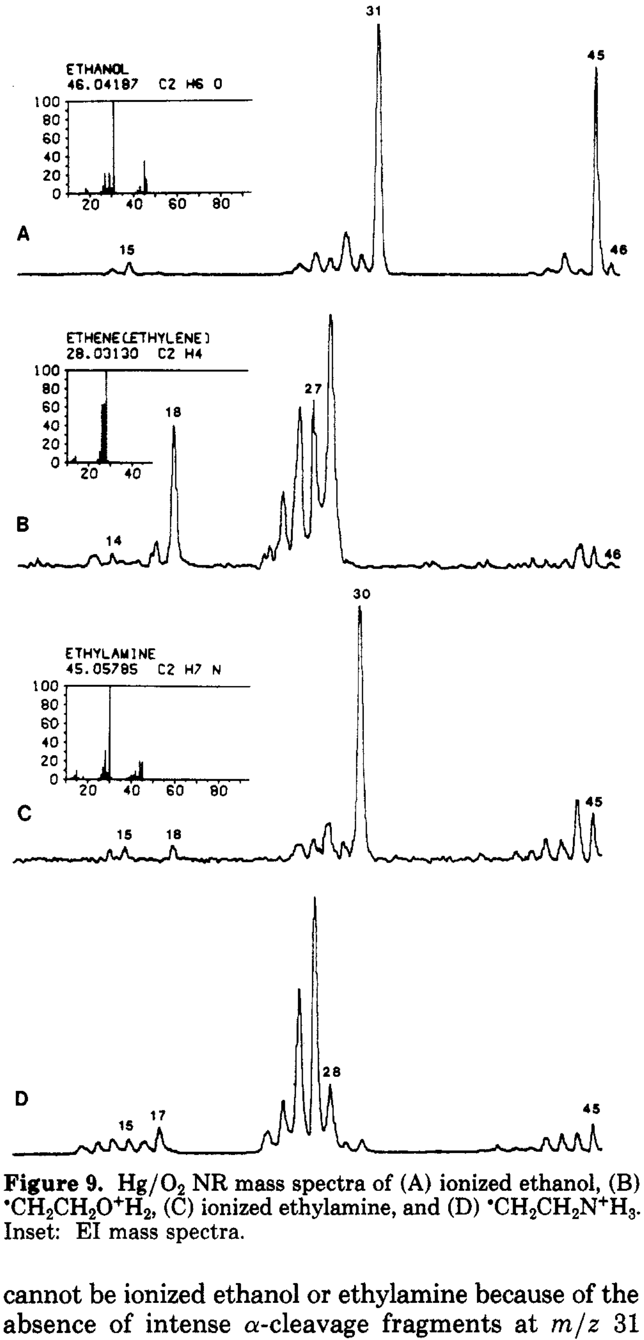


Figure 9. Hg/O_2 NR mass spectra of (A) ionized ethanol, (B) $^{\bullet}CH_2CH_2O^{+}H_2$, (C) ionized ethylamine, and (D) $^{\bullet}CH_2CH_2N^{+}H_3$. Inset: EI mass spectra.

cannot be ionized ethanol or ethylamine because of the absence of intense α-cleavage fragments at m/z 31 (CH_2OH^+) and 30 ($CH_2NH_2^+$), expected from parts A and C of Figure 9. These appear to be reionized $CH_2CH_2OH_2$ and $CH_2CH_2NH_3$ that survived the $\sim 10^{-6}$ s between Hg neutralization and O_2 reionization. The structure of these neutral molecules could resemble a zwitterion, (-)CH_2CH_2YH(+) (Y = OH and NH_2), or an ethylene···YH complex.

4. Hypervalent Radicals

Porter and co-workers prepared fast CH_5, H_3O, NH_4, CH_3OH_2, CH_3NH_3, and H_2F radicals by neutralization of the corresponding positive ions.[7,10,11,29,92-97] These hypervalent species dissociate in $\ll 10^{-7}$ s (e.g., NH_4 lifetime < 150 ns),[7,94] preventing thus mass spectrometric observation. However, perdeuteriation at the heteroatom (e.g., CH_3ND_3) or clustering (e.g., $NH_4(NH_3)_2$) can change dramatically their lifetimes (>20 μs for ND_4), allowing for their characterization via reionization (Figure 10A vs. Figure 10B). The stability of the deuteriated samples is due to the lower zero point energy of N–D vs. N–H bonds, while clustering stabilizes these through H bonding.[11] The ionization energies of these radicals have been determined by evaluating the kinetic energy released upon their dissociation; for the ammoniated radicals the IE values range from 4.7 eV for NH_4 to <3 eV for $NH_4(NH_3)_4$, a value less than the ionization energy of cesium. A theoretical explanation for the stability of the NH_4 Rydberg radical has just been published.[97]

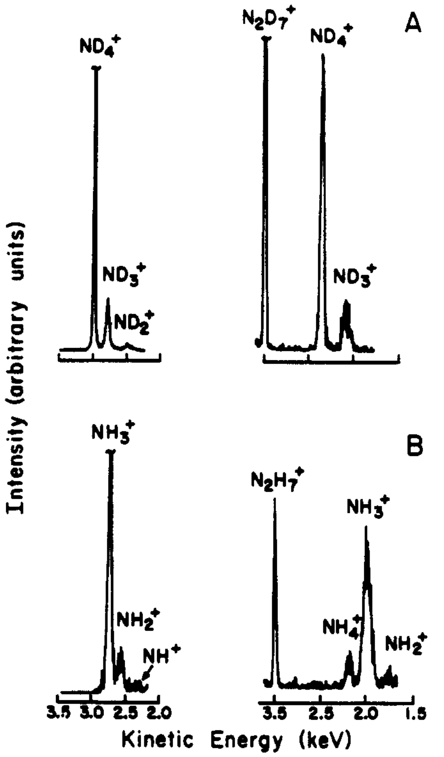
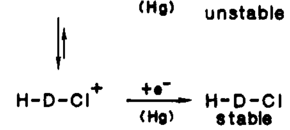


Figure 10. Na/NO_2 NR spectra of (A) ND_4^+ and $ND_4(ND_3)^+$ and (B) NH_4^+ and $NH_4(NH_3)^+$.

Besides H_3,[25b] the simplest nonperdeuteriated hypervalent radical yet found with a significant lifetime for experimental observation is H_2Cl, produced from H_2Cl^+ ions formed in a chemical ionization ion source from HCl.[21] Surprisingly, in the NR mass spectra of the isotopically labeled precursors [$DHCl^+$] ≫ [H_2Cl^+] > [D_2Cl^+], and these abundances are substantially dependent on the chemical ionization source pressure (Figure 11). A possible explanation[21] is that the $HClH^+$ structure initially formed[98] yields an unstable HClH neutral. However, $HClH^+$ may rearrange under low-pressure conditions (absence of thermalizing collisions) to a more stable isomer (eq 11; a variety of geometries are possible for each structure), which on neutralization yields a stable chloronium radical, presumably HHCl.[99,100] Consistent with this, HDCl dissociation (Figure 11E) gives a higher [Cl]/[HCl + DCl] ratio than does dissociation of DClH (Figure 11G). The isomerization $HClH^+ \rightarrow HHCl^+$ would be slowed by perdeuteriation but little by monodeuteriation (eq 11); on the other hand, for the neutral HHCl product the isotope effect should reduce the dissociation of either HDCl or DCl.



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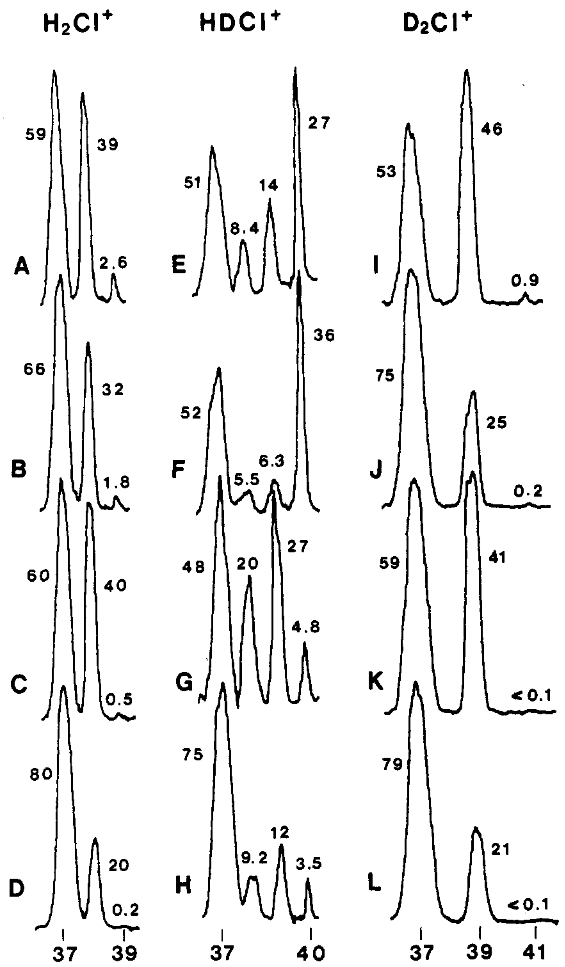


Figure 11. Hg/He NR mass spectra of $H_2{}^{37}Cl^+$ (A–D), $DH^{37}Cl^+$ (E–H), and $D_2{}^{37}Cl^+$ ions (I–L) at lower ion source pressures ($[H_2Cl^+]/[HCl^{\bullet+}]$ = 0.04 (A, E, I, B, F, J)) or higher source pressures ($[H_2Cl^+]/H_2Cl^{\bullet+}]$ = 3.1 (C, G, K, D, H, L)). He reionization was achieved at transmittances of the neutral beams of 90% (A, E, I, C, G, K) and 30% (B, F, J, D, H, L). The figures adjacent to peaks give peak areas as percentage of the spectrum total.

Overall, HDCl should be favored over either H_2Cl or D_2Cl as indeed observed (Figure 11A,E,I).[21] Semiempirical calculations indicate that neutral HHCl is indeed more stable than HClH;[99] however, preliminary higher level ab initio studies have found so far only $HClH^+$ and HClH as true potential energy minima.[100]

An unexpected isotope effect is also observed for the H_3O radical. Isotopically labeled oxonium radicals show apparent stabilities in the order $D_3{}^{16}O \gg D_3{}^{18}O \approx H_3O$; due to their small lifetimes ($<10^{-7}$ s), $D_3{}^{18}O$ and H_3O do not survive neutralization to yield observable precursor ions upon reionization. Clustering improves dramatically the radical stability, so that now both $D_5{}^{18}O_2$ and $H_5{}^{18}O_2$ can be detected.[96] Porter suggests[96] that these and the above chloronium species could be vibrationally bound molecules.

5. Odd-Electron Neutrals (Radicals)

Organic free radicals are highly reactive species, undergoing abstraction, insertion, and polymerization with facility, and often occurring as reactive intermediates.[101] They are usually observed as a minor component of a mixture in the gas phase or in a low-temperature matrix.[102] Charge-exchange neutralization of even-electron ions,[1] formed by appropriate molecular ion dissociations, opens a new route for preparation of radicals free from matrix effects and bimolecular reactions.

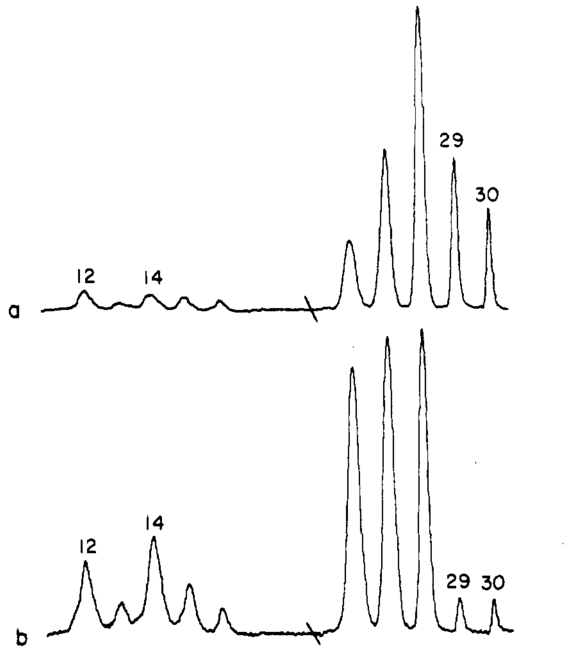


Figure 12. NR mass spectra of $^{\bullet}CH_2NH_2$ with reionization at 30% transmittance by (a) O_2 and (b) He.

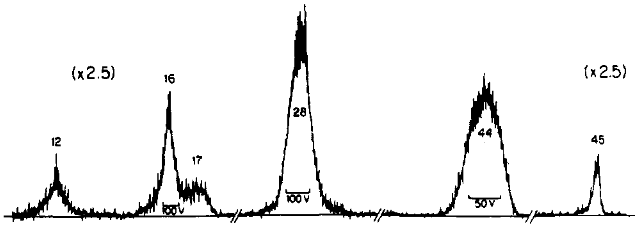


Figure 13. Xe/He NR spectrum of $COOH^+$ ions. The energy resolution is shown for each section in volts.

Radicals generated and characterized via NRMS include $CH_3^{\bullet}$,[20] $C_2H_5^{\bullet}$,[20] $C_3H_7^{\bullet}$,[9] $C_4H_9^{\bullet}$,[15] $C_7H_9^{\bullet}$,[5] $^{\bullet}CH_2NH_2$,[16,33] $^{\bullet}CH_2OH$,[20] $^{\bullet}CH_2F$,[19] $^{\bullet}CH_2Cl$,[16,19,33] $^{\bullet}CH(CH_3)OH$,[103] $^{\bullet}CH_2CH_2OH$,[103] $^{\bullet}CH(CH_3)NH_2$,[9] $^{\bullet}CH_2CH_2NH_2$,[9] $^{\bullet}CH_2CH_2CH_2CH_2OH$,[9] $HCO^{\bullet}$,[18] $DCO^{\bullet}$,[96] $CH_3CO^{\bullet}$ (Figure 3C),[15,18] $(CD_3)_2COD^{\bullet}$,[96] $^{\bullet}COOH$,[18] and $^{\bullet}COOD$.[96] The potential of NRMS to generate and study organic free radicals is demonstrated by the simple radicals aminomethyl and carboxy.

$^{\bullet}CH_2NH_2$ is produced by Hg neutralization of $CH_2{=}NH_2{}^+$, readily obtained upon electron ionization of CH_3NH_2 or $HOCH_2CH_2NH_2$.[16,33] Its reionization with O_2 and with He yields the NR spectra of Figure 12. The presence of reionized parent radicals at *m/z* 30 indicates the expected stability of the neutral species. The predominance of *m/z* 28 is consistent with the thermochemistry of the ion and the neutral: loss of H_2 is the minimum energy dissociation for both species;[39,75,104–106] on the basis of the spectra of $CH_2{=}ND_2{}^+$ this reaction proceeds mainly through 1,2 H_2 elimination.[103]

The Xe/He NRMS of $COOH^+$ from formic acid is shown in Figure 13.[18] Although it is dominated by the fragment ions $CO_2{}^{\bullet+}$ (*m/z* 44) and $CO^{\bullet+}$ (*m/z* 28), the appearance of a well-defined *m/z* 45 peak ($COOH^+$) proves that the carboxyl radical is stable for the time scale of the experiment. The broad peaks at *m/z* 44, 28, and 17 originate from the unimolecular dissociations of $^{\bullet}COOH$ into $CO_2 + H^{\bullet}$ ($\Delta H_f^{\circ} = -42$ kcal mol^{-1})[39] and $CO + OH^{\bullet}$ (−17 kcal mol^{-1}),[39] while the narrower peaks at m/z 12 and 16 (and the narrow Gaussian component of m/z 44) result from fragmentation after reionization.[18] For the $H^{\bullet}$ loss to compete with $CO + OH^{\bullet}$ formation, the dissociation energy of the COO–H bond must be similar to D(CO–OH), in line with theoretical calculations.[107]

Surprisingly, the Zn/NO_2 NR spectrum of $COOD^+$ produced by chemical ionization of CO_2 with D_2 shows no parent ion.[96] Although the $COOD^+/Zn$ reaction is a near-resonant process, only dissociative states are formed now upon neutralization. The different behavior of $COOH^+$ and $COOD^+$ probably lies in the different internal energies of the precursor ions, causing a more unfavorable Franck–Condon factor for the vertical $COOD^+ \rightarrow {}^{\bullet}COOD$ transition than for $COOH^+ \rightarrow {}^{\bullet}COOH$ (vide infra).[20,29]

6. Other Neutral Molecules

Ethynol, $HC{\equiv}COH$,[17] and ethynamine, $HC{\equiv}CNH_2$,[108,109] prepared by neutralization of $HC{\equiv}COH^{\bullet +}$ (from $HC{\equiv}CCO_2H$), and $HC{\equiv}CNH_2^{\bullet +}$ (from $HC{\equiv}CCONH_2$), respectively, have been found to exist as stable neutral molecules in the gas phase, confirming theoretical predictions that both lie in deep potential energy minima.[17,108] Similarly, the disubstituted acetylenes $HOC{\equiv}COH$, $H_2NC{\equiv}CNH_2$, and $H_2NC{\equiv}COH$ produced by Xe neutralization of their radical cations (from squaric acid derivatives) also survive neutralization to yield upon He reionization spectra that are closely similar to the CAD spectra of their precursor ions.[110] Finally, the long-sought free carbonic acid, HOCOOH, and carbamic acid, H_2NCOOH, are available in the gas phase via neutralization from their stable radical cations that Schwarz et al. could recently generate from ammonium carbonate and ammonium carbamate, respectively.[111]

There is no doubt that with NRMS many other fascinating small neutrals which do not exist in solution because of solvent-induced isomerizations[112] will become accessible in the gas phase.

C. Determination of Ion Structures

The charge-exchange neutralization and reionization of organic cations can provide new information on the structure of the ions. Neutralization can make possible a dissociation pathway that is more definitive for structure determination or can reduce collisionally activated isomerization by lowering the barrier for dissociation relative to that for isomerization.

1. Molecular Ions

The NR spectra of many molecular ions from stable neutral molecules are very similar to the corresponding EI spectra, indicating that the sequence of neutralization and reionization involves little change in the original structure. Examples include acetone,[5] ethylamine,[9] methanol,[19] benzene,[18] and acetic acid,[18] all molecules with nonbonding and/or π-electrons.

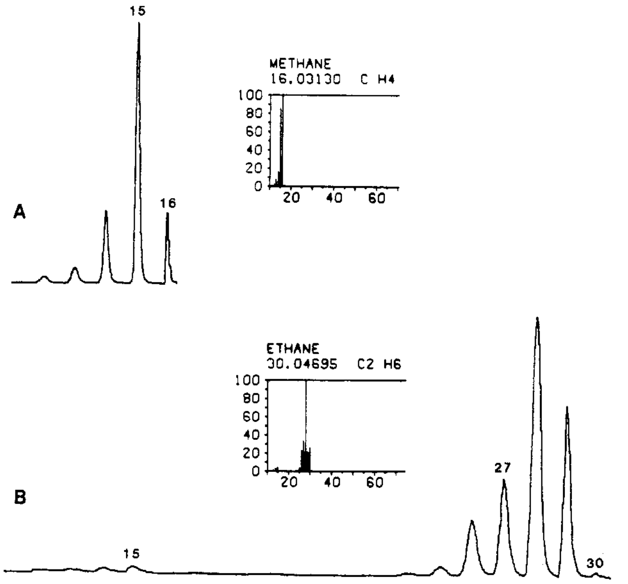
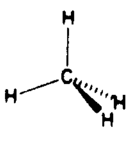


Figure 14. Hg/O_2 NR spectra of (A) $CH_4^{\bullet +}$ and (B) $C_2H_6^{\bullet +}$. Inset: EI spectra.

The situation is different with methane, ethane (Figure 14),[20] and other saturated hydrocarbons, where the abundance of the precursor ion is substantially smaller in the NR than in the corresponding EI spectrum, suggesting extensive dissociation upon neutralization–reionization. The ionization energy (IE) of CH_4 is 2.2 eV above that of mercury,[39a] so that vertical Hg neutralization of $CH_4^{\bullet +}$ should produce neutrals with higher internal energies (see Neutralization).[15,29] However, the ΔIE value of 51 kcal mol^{-1} is far below 104 kcal mol^{-1}, the energy required for the lowest energy dissociation of CH_4 into $CH_3^{\bullet} + {}^{\bullet}H$.[39c] The internal energy of the incipient neutral formed upon charge exchange (eq 1) also depends on the Franck–Condon factor[1,11,29] of the neutralization process, which because of the very short time scale (~10^{-15} s)[11] for electron transfer must be treated as a vertical transition. If the equilibrium structure of the neutral product is distorted from that of its precursor ion, vertical neutralization can leave the neutral with so much internal energy that molecular breakup can take place. Even if no neutral dissociation takes place before reionization, the higher internal energy available would cause a more extensive fragmentation on collision or after reionization. Consequently, the data of Figure 14 indicate substantial structural differences between the neutral molecules and the molecular ions of methane and ethane, in agreement with recent ab initio calculations.[113] These show that CH_4 has T_d symmetry, while for $CH_4^{\bullet +}$ a C_{2v} structure with two long C–H bonds is the only significant minimum on the $CH_4^{\bullet +}$ ab initio potential energy surface. Such substantial changes in structure accompanying ionization are also reflected by large differences between vertical and adiabatic ionization energies.[113,114]



T_d

C_{2v}

Significant differences of structure and geometry between ion and counter neutral, and hence, unfavorable Franck–Condon factors, should be expected not only in alkanes but generally whenever ionization (neutralization) takes place by removal (addition) of

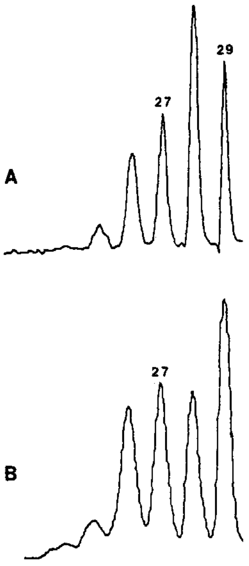


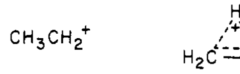
Figure 15. (A) Hg/O_2 NR spectrum of 5-keV $C_2H_5^+$ ions from C_2H_5I. (B) He/O_2 NR spectrum (partial) of 10-keV $CH_3CH_2CH_2NH_2^{\bullet+}$ ions.

σ-bonding electrons, as in CH_3F.[19,115] On the other hand, molecules bearing nonbonding or π-electrons have much more similar EI and NR spectra.

Paralleling electron ionization,[1] the collisional reionization process in NRMS should also represent a vertical transition and could affect in a similar way the internal energy of the reionized molecules. Differences between EI and NR spectra may also result from formation of different populations of ground and excited electronic states upon electron ionization vs. ionization by collision.

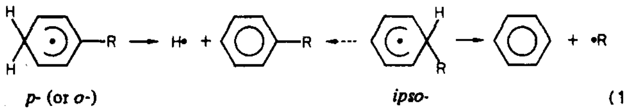
2. Even-Electron Ions

Theoretical[116] and experimental[117] studies disclose that even-electron (EE) ethyl cations can exist in two structures, a classical ($CH_3CH_2^+$) and a more stable bridged ($CH_2HCH_2^+$) structure. Because of the very small interconversion barrier of ≤5 kcal mol^{-1},[117] compared to the dissociation threshold of ~60 kcal mol^{-1} (to $C_2H_3^+$ + H_2),[118] these two forms cannot be distinguished on the basis of CAD spectra. Neutralization, however, freezes this equilibrium, as for the corresponding neutral system only the classical $CH_3CH_2^\bullet$ structure exists, while the bridged $CH_2HCH_2^\bullet$ conformation represents a dissociative state lying ~50 kcal mol^{-1} higher in energy than that for $C_2H_5^\bullet$.[119,120]



Electron ionization of C_2H_5I produces a mixture of classical and bridged cations,[117,121] the relative concentrations of which have been determined by comparing the NR spectrum of ethyl cations from C_2H_5I (Figure 15A) with the reionization spectrum of $C_2H_5^\bullet$ radicals produced by CAD of $CH_3CH_2CH_2NH_2^{\bullet+}$ (He/O_2 NRMS of $CH_3CH_2CH_2NH_2^{\bullet+}$, Figure 15B). Vertical charge-exchange neutralization of the bridged component $CH_2HCH_2^+$ gives bridged radicals that spontaneously dissociate into C_2H_4 + $H^\bullet$,[119-121] reducing thus the $C_2H_5^+$ abundance in the Hg/O_2 NR spectrum of Figure 15A relative to that observed in the reference spectrum of pure ethyl radicals (Figure 15B).[20] The absolute abundance of m/z 29 from reionization of the neutrals produced upon $C_2H_5^+$ neutralization is only $^1/_3$ of [m/z 29] from an identical amount of pure $C_2H_5^\bullet$ radicals. Further, the vertical electron affinities of the classical and bridged $C_2H_5^+$ cations are 8.4 and 6.2 eV, respectively,[121] indicating a better Hg neutralization efficiency for the classical isomer;[15] consequently, the aforementioned absolute NRMS data are consistent with formation of a mixture of <$^1/_3$ classical and >$^2/_3$ bridged $C_2H_5^+$ ions upon electron ionization of C_2H_5I.[20]

Neutralization of an EE^+ ion produces an odd-electron neutral whose specific "radical site" dissociations[1,101] are more definitive for structure determination than the fragmentations of the ion. The site of gaseous protonation in alkylbenzenes could not be defined from conventional CAD spectra, as the $RC_6H_5H^+$ ions from ipso and ortho or para protonation gave similar spectra.[122] However, dissociation of the corresponding neutral isomers to yield aromatic molecules (eq 12) is more selective. Consistent with the dominant ortho- or para-protonation observed in solution,[123] the Hg/He NR spectrum of the $C_7H_9^+$ ions from protonation of toluene shows insignificant (<5%) CH_3 and C_6H_6 peaks and is closely similar to the NR spectrum from ionized toluene.[5] $C_7H_9^\bullet$ partly survives neutralization, indicating that the methylbenzenium radical is stable; such radicals appear as intermediates in the Birch reaction.[124]



(12)

While only the ionic fragment of an ion dissociation is recorded in conventional mass spectra,[1-3] a NR spectrum includes all dissociation products. For example, in the Hg/He NR spectrum of $CH_3OH_2^+$, CH_3^+ and $H_2O^{\bullet+}$ ions are observed, originating from the dissociation of the hypervalent $CH_3OH_2^\bullet$ oxonium radical into $CH_3^\bullet$ + H_2O. EI, CI, or CAD spectra do not give such a direct characterization of the hydroxyl group (Stevenson's rule).[1]

3. Distonic Radical Ions

Distonic[90] radical ions have separated radical and charge sites and are formed upon rearrangement dissociations of larger radical ions.[9,78] The Hg/O_2 NR spectra of the oxonium ion $^\bullet CH_2CH_2OH_2^+$ and the ammonium ion $^\bullet CH_2CH_2NH_3^+$ are shown in parts B and D of Figure 9, respectively, along with the spectra of their conventional isomers $CH_3CH_2OH^{\bullet+}$ (Figure 9A) and $CH_3CH_2NH_2^{\bullet+}$ (Figure 9C).[9] The NRMS data of Figure 9A,B clearly prove that ionized ethanol and $^\bullet CH_2CH_2OH_2^+$ do not interconvert in the microsecond time scale of the experiment, in agreement with CAD results.[125] The main peaks in the NR spectrum of $^\bullet CH_2CH_2OH_2^+$ are consistent with the products from the exothermic dissociation of $^\bullet CH_2CH_2OH_2^\bullet$ ($CH_2{=}CH_2$ + H_2O),[39] matching the EI mass spectra of ethylene and water.

For $^\bullet CH_2CH_2NH_3^+$, one main fragmentation path upon collisional activation involves rearrangement to ionized ethylamine followed by α-cleavage to $CH_2{=}NH_2^+$ (m/z 30).[126] This reaction is misleading for structural analysis, since it also is the major dissociation channel of $CH_3CH_2NH_2^{\bullet+}$.[126] However, charge-exchange neutralization of $^\bullet CH_2CH_2NH_3^+$ bypasses this problem by yielding $^\bullet CH_2CH_2NH_3^\bullet$, whose dissociation energy to C_2H_4 + NH_3 must be appreciably below its energy of isomerization to $C_2H_5NH_2$ (on the basis of the abundance of m/z 30 in Figure 9C,D), an obvious advantage of NR over CAD mass spectra for ion structure characterization.

The intense $C_2H_3^+$ ion (m/z 27) in the NR spectrum of Figure 9D results from reionization of $C_2H_3^\bullet$ formed upon CAD/Hg of $^\bullet CH_2CH_2NH_3^+$ (dissociative neutralization accompanying charge-exchange neutralization). Saturated ammonium ions often show higher cross sections for CAD (eq 2) relative to that for charge exchange (eq 1).[9,40]

Neutralization–reionization spectra of the larger distonic ions $^\bullet CH_2(CH_2)_nXH^+$ (X = OH and NH_2; n = 2 and 3) have been also measured[9] and reveal that the isomerization $CH_3(CH_2)_nX^{\bullet+} \rightarrow {}^\bullet CH_2(CH_2)_nXH^+$ is more exothermic for X = OH but has a lower activation energy for X = NH_2, consistent with previous conclusions that radical site reactions at nitrogen are favored.[1] For this isomerization, a 1,5 H rearrangement is preferred over 1,4, while 1,3 H (Figure 9) and 1,5 H rearrangements were not observed, confirming labeling experiments.[127–131]

D. Studies on Multiply Charged Ions and Negative Ions

1. Multiply Charged Cations

Charge stripping (CS) spectra, obtained by collision of fast monocations with gaseous targets (eq 13) to

$$\bar{M}^+ + A \rightarrow \bar{M}^{2+} + A + e^- \qquad (13)$$

$$\bar{M}^{2+} \rightarrow m_1^{2+} + m_2, m_3^+, + m_4^+, ... \qquad (14)$$

$$\bar{M}^+ \rightarrow (1/2m_1)^+, m_3^+, ... \qquad (15)$$

$$\bar{M}^{2+} + C_6H_6 \rightarrow \bar{M}^+ + C_6H_6^{\bullet+} \qquad (16)$$

produce doubly charged cations that can then dissociate (eq 14), have found extensive use in differentiating between isomeric structures of organic ions.[46,47,132] An intrinsic problem of this technique, however, arises from overlapping of CS peaks with peaks from dissociation of the singly charged ion (eq 15). A technique that is free from such interferences combines charge stripping with charge exchange (CE) in a triple-sector BEE or BEB mass spectrometer.[133] Ions are charge stripped with N_2 in the second field-free region and then subjected to a charge-exchange reaction with C_6H_6 targets in the third field-free region (eq 16). Appropriate setting of the second electric sector voltage rejects all interfering singly charged ions, and only $\bar{M}^+$ from reaction 16 and its fragments are transmitted. The charge stripping/charge exchange (CS/CE) spectra of $C_6H_6^{\bullet+}$, $C_6H_5^+$, $C_8H_{10}^{\bullet+}$, and $C_7H_7O^+$ ions from a variety of precursors have been recorded;[133] in most cases, sufficient differences are observed to permit distinction between isomeric structures.

2. Negative Ions

Neutralization of a negative ion can take place unimolecularly or, with better yields, upon collisional activation.[12,23] Reionization of the resulting neutrals can provide valuable reference spectra for structures that do not exist as positive ions, e.g., RO^+. The NR spectra of CH_3O^-,[12] $C_3D_7O^-$,[23] CH_3^-,[12] and $C_6H_5NO_2^-$ [12] have been reported; they are similar but not identical with the respective charge reversal spectra,[70] which might indicate energy effects.

A thorough charge inversion and NRMS study of Harrison and co-workers[23b] on C_1–C_3 alkoxide ions reveals that He, N_2, and O_2 show similar efficiencies for collisional charge inversion and produce similar mass spectra, although fewer high-energy oxenium ions are formed when O_2 and N_2 are used as collision gases. The NR mass spectra obtained with a variety of neutralization (Xe, O_2, N_2, and He) and reionization (O_2, N_2, and He) targets are in general agreement with the direct charge inversion spectra, indicating that mainly alkoxy radicals are produced, although, particularly with Xe and He as neutralization collision gases, additional neutrals are formed. As the size of the alkoxy group increases, neutral fragmentation reactions prior to reionization become more prevalent. The authors find He as the most suitable collision gas for charge inversion and suggest the combination O_2/He as the most suitable for neutralization–reionization of negative ions.[23]

Our current investigations[22,71] show that oxygen is a much more efficient (than He or N_2) target gas for the collisional conversion of fast positive ions to negative ions, while Xe, CH_3OH, and benzene are even better for the conversion $CH_3O^\bullet \rightarrow CH_3O^-$. This appears to provide an advantageous way to characterize species whose negative ions are stable; such species could be negative ions, neutrals, or positive ions that can be converted to neutrals for negative ionization.

V. Conclusions and Future Prospects

Neutralization–reionization mass spectrometry extends the ability of mass spectrometry to investigate the chemistry of fast neutral and ionic organic species. Information is obtained on the structure, lifetime, and stability of the neutral species and on the structure of the precursor ion.

The preparation and characterization of unstable and reactive neutrals is possible with NRMS. Reference spectra of neutral species can be prepared with NRMS, and in comparison with the spectrum of the neutral product of an ionic dissociation the structure of the neutral dissociation product can be determined, aiding in the postulation of decomposition mechanisms. NR mass spectra also provide information on ion structures in addition to that from CAD; this can be very useful in cases where neutralization freezes the facile interconversion of ionic isomers that often occurs upon CAD. Although neutralization and reionization are accompanied by a substantial loss in sensitivity, this is partially offset by the accompanying reduction in "chemical noise",[3] so that useful data can be obtained routinely by utilizing Hg neutralization and O_2 reionization.

All studies so far have been completed with instruments modified to accommodate NRMS. A good sector mass spectrometer for NRMS should have differential pumping for the neutralization/neutral CAD/reionization chambers to avoid interferences in these regions and a long and variable distance between collision cells to allow kinetic studies of the neutrals. Direct detection of neutral fluxes is essential for quantitative studies; a direct way to determine the composition of the neutral beam before reionization would therefore be desirable (possible with Porter's instrumentation),[29] in addition to modifications in MS-II that will improve the collection efficiency of small fractional masses. Photoreionization should provide much more accurate measurement of IE values of numerous unstable neutrals; measurement of their photoelectron spectra is conceivable.

NRMS experiments can also be compatible with Fourier transform (FT) MS instruments by using multiply charged precursor ions, transforming them into less charged products.[24] Neutralization of one of the charge sites of a multiply charged cation with an electron could cause rapid, possibly nonergodic, cleavage at that site giving ionized product ions that can easily be detected in the FTMS cell.

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