

# Neutralization–Reionization Mass Spectrometry: A Powerful “Laboratory” To Generate and Probe Elusive Neutral Molecules

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## Introduction

At first sight, the suggestion to study neutral species by mass spectrometric techniques might seem a contradiction inasmuch as, in conventional mass spectrometry, only *ionic* species are analyzed. However, the discovery by Lavertu et al.<sup>1</sup> in 1966 that fast ionic beams can undergo charge exchange upon collision with a neutral target gas, to form beams of *neutral* molecules, opened up a new field to probe the gas-phase chemistry of neutral species by means of mass spectrometric techniques. Richard Porter and co-workers soon exploited the neutralized ion beam method for the investigation of a great many di- and triatomic radicals,<sup>2</sup> including stable Rydberg states of  $H_3^+$ . Nevertheless, the potential of this method was not fully recognized until the laboratories of McLafferty<sup>3a</sup> and others<sup>3b,4</sup> pioneered the field with their studies on polyatomic organic intermediates. Within a relatively short period the technique of neutralization–reionization mass spectrometry (NRMS) has become a powerful tool for the generation and identification of numerous elusive species.<sup>4</sup> This research area had previously been limited to either matrix isolation or the spectroscopy of jet-cooled molecules.

NRMS has three major advantages when compared with other experimental approaches used in the detection of transient species. First, no solvent or cage effects interfere as the gas-phase experiments are conducted in the high vacuum existing in a mass spectrometer. Second, all techniques for ion preparation can be employed to produce a precursor ion of interest; other methods applicable for the observation of reactive short-lived species are often restricted to photochemical or thermal generation of the intermediates. Third, the internal energy content of the neutral N generated in the charge transfer process (Figure 2) can be controlled to some extent by choosing the collision target T.<sup>2–4</sup>

A schematic representation of a neutralization–reionization experiment is depicted in Figure 1. In a

typical experiment, a beam of mass- and energy-selected ions<sup>5</sup> possessing translational energies in the 4–10-keV range collides with a neutral target gas (a variety of gases are in use, e.g., Xe, Hg, Na, Zn,  $NH_3$ , NO, or organic neutralization agents, etc.)<sup>6</sup> under near-single-collision conditions (see Figures 1 and 2). A small fraction of these ions undergo a charge-exchange reaction leading to a mixed beam of neutral and ionic molecules. “Purification” of the beam is then accomplished electrostatically by charging an electrode that deflects all ionic species from the mixture (see Figure 1). The neutral beam continues its journey and enters a second collision cell, where a fraction of the neutral species is reionized upon collision with a second target gas, such as oxygen. The ionization energy necessary for the transformation  $N \rightarrow I^+$  is delivered by the kinetic energy of the fast moving beam. Typically, in a NR spectrum the survivor-ion abundance is about  $10^3$ – $10^5$  times smaller than that of the original ion beam. The reionized beam is then analyzed by using an additional sector or can be subjected to further collision experiments. If, in the mass spectrum obtained upon reionization of the neutralized species, a signal corresponding to the reionized parent ion (*survivor signal*) is observed, this immediately demonstrates that the neutral species must correspond to a bound state on the time scale of the experiment.<sup>7</sup> However, a problem occurring in polyatomic systems concerns the structural homogeneity of the ionic precursor beam as well as possible rearrangements of the neutrals prior to reionization. Therefore, it has proven extremely helpful (and in some cases mandatory) to use supplementary *ab initio* MO calculations that render insight into possible

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(2) Gellene, G. I.; Porter, R. F. *Acc. Chem. Res.* **1983**, *16*, 200.

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(4) (a) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (b) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *8*, 513. (c) McLafferty, F. W. *Science* **1990**, *247*, 925. (d) McLafferty, F. W. *Int. J. Mass Spectrom. Ion Processes* **1992**, *118/119*, 221. (e) Turecek, F. *Org. Mass. Spectrom.* **1992**, *27*, 1087.

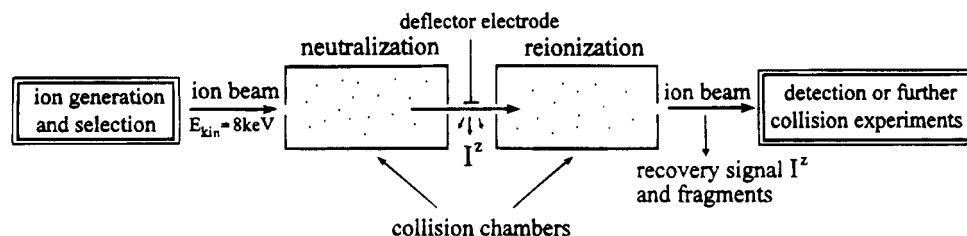
(5) In general, selection of the precursor ion is accomplished by using a magnetic (B) or an electrostatic analyzer (E), and preferably both. The sectors are located in front of the collision cells of a multisection mass spectrometer.

(6) It should be noted that only “non-momentum-transfer collisions”, which leave the original direction of the investigated species largely unchanged, will lead to a detectable signal in this experimental setup. This is one of the reasons why the primary ion beam intensity in a NRMS experiment decreases drastically.

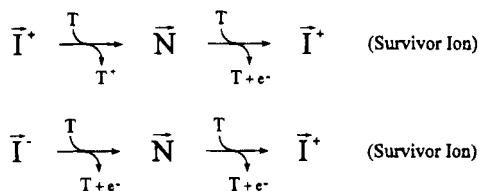
(7) In a conventional NRMS experiment the *minimal lifetime*  $\mu$  for the neutral molecule can be easily derived from the flight time it takes the neutrals to travel from the neutralization to the reionization chamber, and  $\mu$  is of the order of a few microseconds.

Norman Goldberg was born in Freiburg, Germany, in 1965 and grew up in Switzerland. He studied chemistry at the Justus-Liebig-University, Giessen, Germany, where he obtained his diploma with a work on matrix-isolation spectroscopy of silicon-containing molecules, under Professor G. Maier. He then entered the exciting field of gas-phase ion chemistry and joined Professor Schwarz's group at the Technical University of Berlin, where he is currently finishing his Ph.D. thesis. Besides chemistry his heart is devoted to the beauty of the Irish countryside and its souls.

Helmut Schwarz's career and interests are described in a previous *Accounts* essay (*Acc. Chem. Res.* **1989**, *22*, 282). More recently he was awarded the Leibniz Research Award of the Deutsche Forschungsgemeinschaft, the Otto Bayer Award, and the Max Planck Research Award (jointly with Chava Lifshitz) of the Alexander von Humboldt-Stiftung. In 1992 he received an honorary degree from the Hebrew University of Jerusalem, and he was elected a Fellow of the Deutsche Akademie der Naturforscher (LEOPOLDINA) as well as the Academy of Sciences Berlin-Brandenburg (the former Prussian Academy of Sciences).



**Figure 1.** Schematic representation of a mass spectrometer used for neutralization–reionization experiments of mass-selected ions  $I^z$  ( $z = +/-$  charges; (see text for discussion)).



**Figure 2.** Neutralization and reionization reactions taking part in the course of the collisions of an ion  $I^z$  ( $z = +/-$ ) with a neutral target gas T, exemplified for a  $+NR^+$  (top) and a  $-NR^+$  experiment (bottom). Other charge permutations are possible as well (see text).

isomerization pathways as well as the barriers for these processes and help to interpret the obtained NR spectra. Another approach is to elucidate the connectivity of the reionized species by performing a subsequent collisional activation (CA) experiment<sup>8</sup> (NRMS-CA), provided that the intensity of the reionized beam permits such an experiment. If the CA spectrum of the source-produced ion is identical to the NRMS-CA spectrum, this unequivocally demonstrates that the neutral species has retained the structure of the precursor ion, which itself has to be inferred from independent mass spectrometric experiments.

A NR mass spectrum of a reionized polyatomic neutral does not only exhibit a survivor signal; in addition, all energetically accessible dissociation products of the neutral species will also be ionized, thus rendering a fingerprint of the neutral's unimolecular chemistry. Positive ions as well as negatively charged species can be investigated by NRMS, and depending on the original charge state of the ions and their reionized species, the experiments are denoted as  $+NR^+$ ,  $+NR^-$ ,  $-NR^-$ , or  $-NR^+$ ; i.e.,  $+NR^-$  refers to the neutralization of a cation followed by reionization to its anion.

An important point in the interpretation of the NR spectra concerns the nature and mechanism of the electron-transfer reactions. These processes have been demonstrated to correspond to approximately *vertical transitions*,<sup>9</sup> and thus their efficiencies are largely controlled by the Franck–Condon factors governing these transitions. An immediate implication of Franck–Condon effects is that, depending on the geometries and relative energies of the examined species, not only the ground state of a molecule but, in a considerable number of cases, rovibronically as well as electronically excited states may be populated in the charge-transfer event.

In the last decade, numerous experimental studies employing the NRMS technique were carried out

(8) Structural information, i.e., connectivities of ions, can be obtained by subjecting species to high-energy collisions with a target gas thus giving rise to a number of structure-indicative ionic dissociation products.

(9) Lorquet, J. C.; Leyh-Nihant, B.; McLafferty, F. W. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 465.

dealing with a wide range of different molecules.<sup>4</sup> In this Account, however, we limit ourselves to a number of recent, outstanding examples that demonstrate the strength of the technique for the investigation of elusive neutral molecules which are believed to play an important role in areas as diverse as interstellar, atmospheric, or organometallic chemistry, to mention a few. For a discussion of experimental details and earlier work (prior to 1992) the reader is referred to several reviews covering these and other aspects.<sup>4</sup>

## NRMS Studies

**Reactive Organic Intermediates.** Structural studies of *carbenes* and *nitrenes* have demonstrated the fruitful interplay between experiment and theory, and several intriguing species recently have been discovered to exist via NRMS.<sup>10–13</sup> Among the vinylidene-type carbenes, molecules that are of particular interest to astrochemists as these species are believed to exist in interstellar matter, cyanovinylidene ( $:C=C(H)CN$ )<sup>10a</sup> and the cumulenic butatrienyldiene ( $:C=C=C=CH_2$ )<sup>10b</sup> have been characterized. These compounds have been generated from their corresponding anionic precursors in  $-NR^+$  experiments. The anions themselves can be obtained in an efficient ion–molecule reaction of the hydrogen-substituted precursor molecules with the oxygen radical anion  $O^{\cdot-}$  ( $H_2CCCCH_2 + O^{\cdot-} \rightarrow H_2C_4^{\cdot-} + H_2O$ ). Terlouw and co-workers have recently shown dihydroxycarbene ( $HOCO$ ),<sup>11a</sup> hydroxyaminocarbene ( $HOCNH_2$ ),<sup>11b</sup> and diaminocarbene ( $H_2NCNH_2$ )<sup>11c</sup> to be viable species in the gas phase. Using NRMS we have been able to demonstrate the existence of aminonitrene ( $H_2NN$ ), the isomer of diimine ( $HNNH$ ), in the dilute gas phase.<sup>12</sup>

Another important class of compounds that has received great experimental as well as theoretical interest is the *cumulenes*,<sup>14–16</sup> molecules of the general structure  $X(C_n)Y$  ( $X, Y = O, S, NH, NR$ , lone electron pair;  $n \geq 2$ ). For example, Mosandl et al.<sup>15a</sup> have reported the observation of iminopropadienones  $RNC-CCO$ . In their study the authors used a flash-vacuum-pyrolysis device coupled to the ion source of a mass spectrometer for the generation of the cumulenes from

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(11) (a) Burgers, P. C.; McGibbon, G. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1994**, *224*, 539. (b) McGibbon, G. A.; Burgers, P. C.; Terlouw, J. K. *Int. J. Mass Spectrom. Ion Processes*, in press. (c) McGibbon, G. A.; Kingsmill, C. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1994**, *222*, 129.

(12) Goldberg, N.; Holthausen, M. C.; Hrušák, J.; Koch, W.; Schwarz, H. *Chem. Ber.* **1993**, *126*, 2753.

(13) Sülzle, D.; Seemeyer, K.; Witulski, B.; Hopf, H.; Schwarz, H. *Chem. Ber.* **1991**, *124*, 1481.

(14) For earlier work on the gas-phase characterization of polycarbon chalcogenides, see: Sülzle, D.; Schwarz, H. In *Fundamentals of Gas Phase Ion Chemistry*; Jennings, K. R., Ed.; Kluwer Academic Publishers: Netherlands, 1991; p 237 and references therein.

heterocyclic precursor molecules. One species that despite a considerable number of experimental attempts has so far escaped its definitive experimental observation and that might well be regarded as the "holy grail" of heterocumulenenic molecules is ethylenedione, OCCO. All collision experiments aimed at generating this simplest of all possible poly carbon dioxide molecules from the readily available cationic precursor OCCO<sup>+</sup> have failed up till now.<sup>16</sup> On the basis of theoretical considerations, the electron-transfer process is believed to lead to the unstable singlet electromer <sup>1</sup>Δ<sub>g</sub> rather than to the bound <sup>3</sup>Σ<sub>g</sub><sup>-</sup> state of the neutral, and this may account for the failure to detect neutral ethylenedione.<sup>16</sup>

**"Elusive" Molecules.** The NRMS technique has provided evidence for the existence of a number of simple acids<sup>11b,17,18</sup> that have so far not been observed in the condensed phase, most likely because of facile intermolecular processes. Wiedmann and Wesdemiotis<sup>18</sup> recently published experimental proof for the existence of fluoroformic acid, FCOOH. In their study these authors made use of a collision experiment prior to the <sup>+</sup>NR<sup>+</sup> experiment in order to generate the cationic precursor FCOOH<sup>+</sup>. Ethyl fluoroformate was observed to form FC(OH)<sub>2</sub><sup>+</sup> cations via a McLafferty +1 rearrangement under electron-impact conditions. Mass-selected FC(OH)<sub>2</sub><sup>+</sup> ions were then collisionally activated, thus yielding the radical cation of fluoroformic acid (FC(OH)<sub>2</sub><sup>+</sup> → FCOOH<sup>+</sup> + H<sup>•</sup>). In a subsequent conventional <sup>+</sup>NR<sup>+</sup> experiment, the radical cation was successfully neutralized to the theoretically predicted FCOOH. A study demonstrating the existence of formimidic acid (HNC(H)OH), which clearly shows the advantages of combined labeling studies with ab initio calculations, has recently been carried out by McGibbon et al.<sup>11b</sup> By probing the structure of the "survivor" ions obtained in the <sup>+</sup>NR<sup>+</sup> sequence through a subsequent collision experiment (NRMS-CA), the authors were not only able to distinguish the two new neutral isomers of formamide (H<sub>2</sub>NC(H)O), i.e., formimidic acid (HNC(H)OH) and aminohydroxycarbene (H<sub>2</sub>NCOH); in addition they were successful in demonstrating that the neutral imidic acid, in contrast to the cationic species, tautomerizes to a certain extent during the <sup>+</sup>NR<sup>+</sup> experiment to its corresponding amidic form, the formamide.

The existence of the higher analogue of hydrogen peroxide (HOOH), the hitherto unknown hydrogen pertelluride (HTeTeH), was recently established by Hop and Medina;<sup>19</sup> this work also demonstrates the validity of NRMS for the study of molecules containing higher main-group elements.

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(16) Sülzle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, 75.

(17) For earlier work on elusive acids, including the celebrated case of carbonic acid, see: (a) Terlouw, J. K.; Lebrilla, C. B.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 345. (b) van den Berg, K. J.; Lebrilla, C. B.; Terlouw, J. K.; Schwarz, H. *Chimia* **1987**, *41*, 122.

(18) Wiedmann, F. A.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1994**, *116*, 2481.

(19) Hop, C. E. C. A.; Medina, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 3163.

### Ylides, Hypervalent Molecules, and Diradicals.

The NRMS technique has proven very useful for the characterization of a number of unusual molecules such as ylides,<sup>20</sup> hypervalent molecules,<sup>21</sup> and diradicals.<sup>22,23</sup> For example, the ylide molecule hydrogen cyanide *N*-methylide (HCN<sup>+</sup>—CH<sub>2</sub>)<sup>20a</sup> or the thioxonium ylide S<sup>-</sup>—<sup>+</sup>OH<sub>2</sub><sup>20b</sup> can be obtained upon one-electron reduction of the corresponding cations.

Among the hypervalent species, several studies have appeared assessing the stability and unimolecular chemistry of these unusual molecules. In a study of the hydrated oxonium radicals H<sub>3</sub>O(H<sub>2</sub>O)<sub>*n*</sub><sup>•</sup> and ammoniated ammonium radicals NH<sub>4</sub>(NH<sub>3</sub>)<sub>*n*</sub><sup>•</sup>,<sup>21a</sup> it was found that the "solvation" of the radicals does lead to an enhanced stabilization of the hypervalent center NH<sub>4</sub><sup>•</sup> and H<sub>3</sub>O<sup>•</sup>. Beranova and Wesdemiotis<sup>21d</sup> have examined the behavior of quaternary ammonium ions and found their neutral analogues R<sub>4</sub>N<sup>•</sup> (R = alkyl, benzyl) to be unstable toward dissociation on the time scale of a NRMS experiment; rather, the authors observed a rupture of one of the N—R bonds upon neutralization of the ions. However, other species such as protonated ethanol (CH<sub>3</sub>CH<sub>2</sub>OH<sub>2</sub><sup>+</sup>) as well as the isomeric protonated dimethyl ether (CH<sub>3</sub>O(H)-CH<sub>3</sub><sup>+</sup>) were found to give a survivor signal in neutralization experiments, thus leaving no doubt that the hypervalent radicals CH<sub>3</sub>CH<sub>2</sub>OH<sub>2</sub><sup>•</sup><sup>21c</sup> and CH<sub>3</sub>O(H)-CH<sub>3</sub><sup>•</sup><sup>21d</sup> are residing in potential wells.

Shaffer and Turecek<sup>21e</sup> have observed an unusual inverse kinetic isotope effect in the dissociation of neutral trimethylammoniumyl hydride. The deuterated species (CH<sub>3</sub>)<sub>3</sub>ND<sup>•</sup> was found to be considerably less stable than the undeuterated (CH<sub>3</sub>)<sub>3</sub>NH<sup>•</sup>: a rather unexpected finding, as most of the hypervalent species known show a noticeable stabilization of their deuterated isotopologues.<sup>21e</sup> Their results were rationalized by theoretical calculations that suggest the neutral hypervalent species to be unstable in the ground state; indeed, the stable species observed in the experiments are proposed to be formed in an excited state. For the latter state, arguments are discussed that are in keeping with a shorter lifetime of the deuterated analogue.

The neutralization of several distonic<sup>24</sup> radical cations has further led to the observation of a number of interesting 1,3- and 1,4-diradicals<sup>22</sup> that, due to their high bimolecular reactivity, have so far escaped all other experimental characterization. That silicon-bearing molecules can also form stable distonic cations that give rise to stable diradical species was demonstrated in a NR study reporting the gas-phase existence of <sup>•</sup>CH<sub>2</sub>OSi<sup>•</sup>, an isomer of silaketene H<sub>2</sub>SiCO.<sup>23</sup>

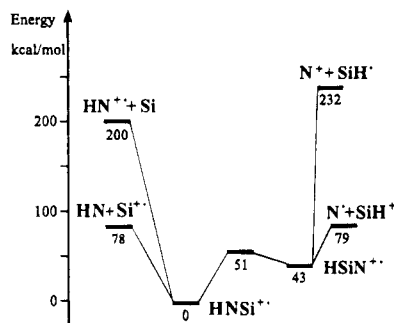
(20) (a) Goldberg, N.; Iraqi, M.; Schwarz, H. *Chem. Ber.* **1993**, *126*, 2353. (b) Iraqi, M.; Schwarz, H. *Chem. Phys. Lett.* **1994**, *221*, 359.

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(22) (a) Wesdemiotis, C.; Leyh, B.; Fura, A.; McLafferty, F. *J. Am. Chem. Soc.* **1990**, *112*, 8655. (b) Polce, M. J.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1993**, *115*, 10849. (c) Polce, M. J.; Houser, J. J.; Wesdemiotis, C. *J. Am. Chem. Soc.*, in press. (d) Shaffer, S. A.; Turecek, F.; Cerny, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 12117.

(23) Srinivas, R.; Böhme, D. K.; Hrušák, J.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1939.

(24) Distonic ions are species in which formally the charge and radical centers are separated. For a recent review, see: Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämää, H. I. *Chem. Rev.* **1992**, *92*, 1649.

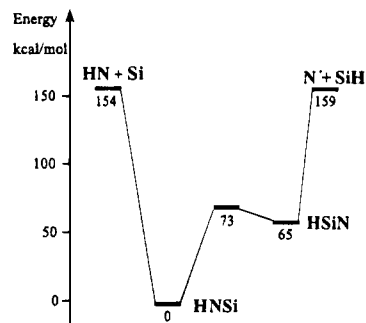


**Figure 3.** Potential energy surface of  $[\text{HNSi}]^+$  (taken from ref 27).

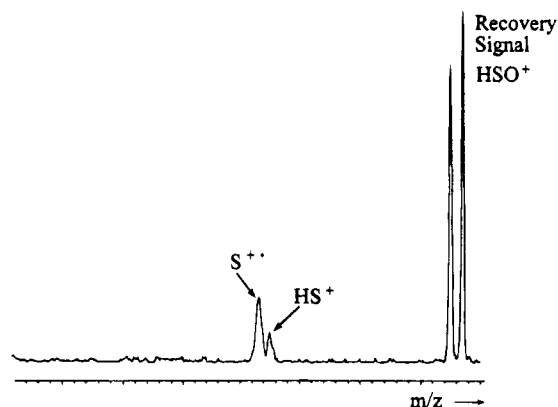
**Interstellar Species.** Chemistry in interstellar space takes place in the highly diluted gas environment of interstellar clouds.<sup>25</sup> Thus, conditions in the high-vacuum chamber of a mass spectrometer are ideal to mimic to some extent an interstellar environment and the physical circumstances responsible for the genesis of *interstellar molecules*. The evolution of bigger molecular species in the intergalactic gaseous clouds is known to be greatly dominated by ion-molecule reactions.<sup>25</sup> This implies that the majority of neutral species generated under these conditions will have ionic precursor molecules.

Among the molecules that have been examined, silicon-bearing species have received special attention, as they are of considerable interest to astrophysicists. Silicon represents a major fraction of the interstellar matter; however, the chemistry of unsaturated silicon compounds is by far not as well understood as that of carbon. This fact is certainly due to the considerably higher reactivity of unsaturated silicon species, thus making them more elusive toward traditional experimental procedures.

A molecule that has received a great deal of interest by experimentalists as well as theoretical chemists is the hydrogen silaisocyanide  $\text{HNSi}$ ,<sup>26,27</sup> the silicon analogue of isocyanic acid (HNC). While the existence of  $\text{HNSi}$  in the interstellar matter is not yet unambiguously proven, the molecule has been shown to be viable in matrix experiments.<sup>26a,b</sup> To the increasing body of circumstantial evidence for the existence of neutral  $\text{HNSi}$  in the gas phase<sup>26c,d</sup> was added definitive experimental evidence provided by NRMS.<sup>27</sup> In addition, theoretical calculations demonstrate that for both the neutral as well as the cationic species the  $\text{HNSi}$  connectivity corresponds to the global minima of the respective potential-energy surfaces (see Figures 3 and 4). Upon examining the  $\text{H}_2\text{NSi}^+$  cation, the nitrogen-protonated form of  $\text{HNSi}$ , by ion-beam techniques, we have also been able to observe the neutral  $\text{H}_2\text{NSi}^{\cdot}$  radical for the first time.<sup>28</sup> Another interesting species worthy of mention in this context is the thionitrosyl hydride molecule ( $\text{HNS}$ )<sup>29</sup>. Here, a situ-



**Figure 4.** Potential energy surface of  $[\text{HNSi}]$  (taken from ref 27).



**Figure 5.**  $-\text{NR}^+$  mass spectrum of  $\text{HSO}^-$  (taken from ref 30b).

ation rather similar to the  $[\text{H,Si,N}]$  system is encountered in that the species possessing the  $\text{HNS}$  connectivities, on both the neutral as well as the cationic potential-energy surfaces, are considerably more stable than the  $\text{NSH}$  isomers.

**Atmospherically Important Molecules.** A number of small sulfur-containing molecules have been investigated that are thought to play an important role in atmospheric processes. Especially in view of the possible decay pathways of anthropogenic as well as natural sulfur-bearing pollutants, several questions have been answered by NRMS studies. For example, the atmospherically abundant bicarbonate  $\text{HOCO}_2^-$  and bisulfite  $\text{HOSO}_2^-$  anions can be oxidized to form the stable  $\text{HOCO}_2^{\cdot}$  and  $\text{HOSO}_2^{\cdot}$  radicals.<sup>30a</sup> One important species that has been suggested to be a key intermediate in a catalytic cycle that depletes ozone in the upper atmosphere is the  $\text{HSO}^{\cdot}$  radical.<sup>30b</sup> Experimental thermochemical data on this species, however, are very scarce in the literature and show discrepancies depending on the measurements. A possible reason for this discordance could well be that, in the experimental studies, the connectivities of the  $[\text{H,S,O}]^{\cdot}$  species produced were not established. NRMS studies that used the anions  $\text{HSO}^-$  and  $\text{SOH}^-$  as precursors indicate two neutral species,  $\text{HSO}^{\cdot}$  along with  $\text{SOH}^{\cdot}$ , to exist as non-interconverting isomers.<sup>30b</sup> As demonstrated in Figures 5 and 6, the connectivities of these two radicals can be directly derived from the NR mass spectra. This finding may point out that the chemistry of the  $\text{SOH}^{\cdot}$  radical also should be taken into account in the kinetic schemes designed for modeling  $\text{O}_3$  depletion.

The chemistry of the dimethyl sulfide ( $\text{H}_3\text{CSCH}_3$ ) molecule, a major natural sulfur source in the atmo-

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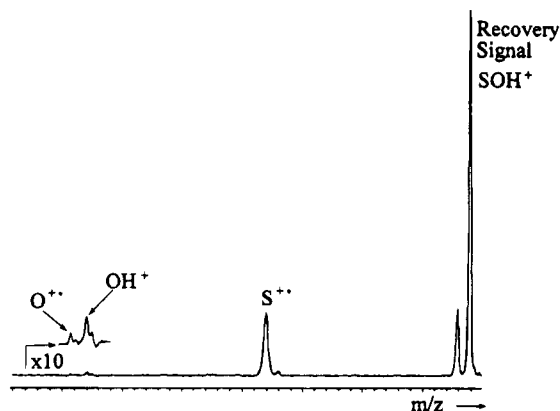


Figure 6.  $^{-}\text{NR}^+$  mass spectrum of  $\text{HOS}^-$  (taken from ref 30b).

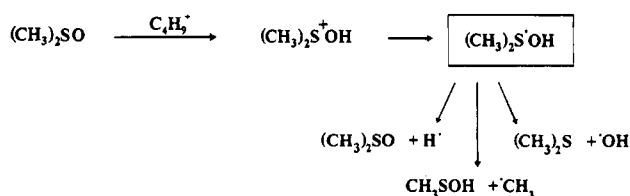


Figure 7. Pathway for the attempted generation of the  $(\text{CH}_3)_2\text{SOH}^+$  radical and its observed unimolecular dissociation products in a NRMS experiment (taken from ref 31a).

sphere, has been thoroughly investigated.<sup>31</sup> NRMS experiments in conjunction with *ab initio* MO calculations have been employed to assess the unimolecular chemistry of the (methylthio)methyl radical ( $\text{H}_3\text{CSCH}_2^{\cdot}$ ).<sup>31c</sup> This species is thought to be the primary product in the atmospheric reaction of photochemically produced  $\text{OH}^{\cdot}$  radicals with dimethyl sulfide. The experiments clearly distinguished between  $\text{H}_3\text{CSCH}_2^{\cdot}$  and two additional species, the  $\text{H}_3\text{CCHSH}^{\cdot}$  as well as the cyclic  $c\text{-H}_4\text{C}_2\text{SH}^{\cdot}$  radicals. The question whether the dimethylhydroxysulfuranyl radical  $(\text{H}_3\text{C})_2\text{SOH}^{\cdot}$  is an intermediate or whether the hypervalent species corresponds to a transition state on the  $\text{OH}^{\cdot} + \text{CH}_3\text{-SCH}_3$  reaction coordinate has been addressed in a further study.<sup>4e,31</sup> The radical  $(\text{H}_3\text{C})_2\text{SOH}^{\cdot}$  formed from protonated dimethyl sulfoxide (Figure 7) was observed to dissociate fully on the time scale of the experiments and, in line with *ab initio* calculations, was found not to correspond to a bound state on the ground-state surface of  $[\text{H}_7\text{C}_2\text{O}_2\text{S}]^{\cdot}$  (Figure 8).

Nitrosamide ( $\text{NH}_2\text{NO}$ ) is a species believed to play a crucial role in a number of atmospheric and combustion reactions.<sup>32</sup> It has been asserted that this molecule is the key intermediate in the reaction of the amidogen  $\text{NH}_2^{\cdot}$  and  $\text{NO}^{\cdot}$ . However, its existence was a matter of controversy for quite a while. NR experiments<sup>32</sup> provided a definitive answer:  $\text{NH}_2\text{NO}^+$  is easily accessible via dissociative ionization of  $\text{H}_2\text{NNO}_2$ , and NR of the former (and its  $^{15}\text{N}$ - and  $^2\text{H}$ -labeled isotopologues) leaves no doubt that  $\text{NH}_2\text{NO}$  is a viable molecule.

**Cluster Molecules.** Among the general topics of cluster chemistry, three different types of clusters

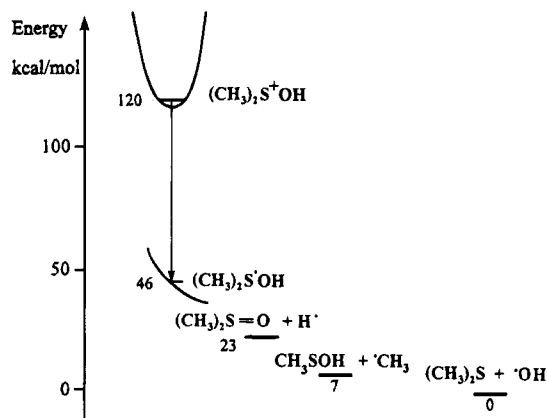


Figure 8. Potential energy surface for the neutralization of protonated dimethyl sulfoxide ( $(\text{CH}_3)_2\text{SOH}^+$ ) to the unbound  $(\text{CH}_3)_2\text{SOH}^{\cdot}$  radical and some of its dissociation products (taken from ref 31a).

have been characterized by applying NRMS. The technique has provided valuable information on the existence and structure of *van der Waals clusters*,<sup>33</sup> *endohedral clusters*,<sup>34</sup> and  *$\sigma$ -bonded cluster molecules*.<sup>35</sup> The *van der Waals* dimer of sulfur dioxide,  $(\text{SO}_2)_2$ , has been examined by  $^{-}\text{NR}^+$  experiments of the anionic dimer  $(\text{SO}_2)_2^{\cdot-}$ .<sup>33</sup> These experiments not only point to a rather strong attractive force between the two neutral  $\text{SO}_2$  molecules but also indicate a second isomer to exist on the presumably rather flat  $[\text{S}_2\text{O}_4]$  surface. Other complexes such as a number of hydrated oxonium radicals  $\text{H}_3\text{O}(\text{H}_2\text{O})_n^{\cdot}$  and ammoniated ammoniated clusters  $\text{NH}_4(\text{NH}_3)_n^{\cdot}$  have been shown to be viable in the gas phase.<sup>21a</sup>

We were able to provide the first unambiguous experimental evidence for the incorporation of rare-gas atoms inside the cage of buckminsterfullerene.<sup>34</sup> The existence of neutral *endohedral*<sup>36</sup> helium–fullerene molecules was established by a sequence of collision experiments. In brief, a 5-keV beam of mass-selected  $\text{C}_{60}^{+\cdot}$  cations was produced and collided with helium atoms in an initial collision event. A considerable number of these  $\text{C}_{60}^{+\cdot}$  ions were observed to form a cluster molecule of composition  $\text{HeC}_{60}^{+\cdot}$ . The  $\text{HeC}_{60}^{+\cdot}$  ions were carefully mass-selected, then neutralized, and subsequently reionized in a second and a third collision, respectively. The presence of a recovery signal for the reionized  $\text{HeC}_{60}^{+\cdot}$  cation unequivocally demonstrated that the neutral cluster was formed in the electron-transfer reaction. This experimental finding shows that the helium atom in the collision with  $\text{C}_{60}^{+\cdot}$  must have penetrated the carbon cage, since a very weakly bound exohedral helium atom cannot retain its position on the fullerene surface during the successive collision processes. The  $\text{He@C}_{60}$  cluster represents the first helium–carbon compound ever made. Results of these gas-phase experiments have only recently been augmented by a beautiful nuclear

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(36) Species that possess a cage-like structure and contain additional non- $\sigma$ -bonded atoms or molecules inside the cavity are generally referred to as *endohedral clusters*.

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magnetic resonance experiment, probing the  $^3\text{He}$  atom inside the  $\text{C}_{60}$  cage.<sup>37</sup>

Several unusual silicon–nitrogen and silicon–oxygen cluster molecules that can be regarded as building blocks for polymeric materials, such as  $\text{Si}_2\text{O}$ ,<sup>35a</sup>  $\text{Si}_2\text{O}_2$ ,<sup>35b</sup>  $\text{Si}_2\text{N}^+$ ,<sup>35a</sup> and  $\text{Si}_3\text{N}^+$ ,<sup>35c</sup> have been characterized by NR. In these combined experimental/theoretical studies, the rather different bonding situation in these highly unsaturated silicon compounds, when compared with their homologous carbon species, is demonstrated.

**Metal-Containing Molecules.** The NR technique is certainly not restricted to the investigation of the chemistry of main-group elements. Several elusive transition-metal species have, for the first time, successfully been characterized in the gas phase by NRMS.<sup>38,39</sup> Upon generating the gold monofluoride cation ( $\text{AuF}^+$ ) from  $\text{AuF}_3$  and subjecting it to NR, we have been able to demonstrate the existence of the long-sought-after gold monofluoride ( $\text{AuF}$ ).<sup>38</sup> In spite of a large experimental effort,  $\text{AuF}$  has not been made in the condensed phase until now. This observation points to facile intermolecular processes in the solid state rather than an intrinsic instability of  $\text{AuF}$ , in perfect agreement with theoretical predictions.

In another study, the bonding principles of simple ligands attached to a neutral as well as cationic iron atoms have been probed.<sup>39a</sup> The cationic iron ethene  $\text{Fe}(\text{C}_2\text{H}_4)^+$  and carbon monoxide  $\text{FeCO}^+$  complexes were reduced to their neutral counterparts so as to gain insight into the unimolecular chemistry of neutral  $\text{Fe}(\text{C}_2\text{H}_4)$  and  $\text{FeCO}$ . This work also demonstrates the strength of a combined theoretical/experimental approach as the neutral  $\text{FeCO}$  cluster was found to be formed in a stable electronically excited state upon electron transfer, and not in its ground state.<sup>39a</sup> In addition, several questions concerning the Franck–Condon factors and particularly the effect of curve crossing in such transition-metal compounds, which are highly probable due to efficient spin–orbit coupling, have been addressed. Similarly, the instability

of neutral  $\text{Fe}(\text{C}_2\text{H}_4)$  in the gas-phase experiments could be explained in a consistent way.

The structure of simple organic ligands attached to the metal center may also be elucidated by NRMS experiments. For example, upon neutralizing the  $\text{Fe}(\text{C}_2\text{H}_2)_3^+$  cation, generated from the iron cation and three acetylene molecules,<sup>39b</sup> it was possible to prove that the iron must have mediated the oligomerization of the acetylenes to form benzene as the spectrum obtained compared rather well to that of a genuine  $\text{Fe}(\text{C}_6\text{H}_6)^+$  complex. In particular, it contains an abundant signal for  $\text{C}_6\text{H}_6^{++}$ , which clearly demonstrates that the three separate  $\text{C}_2\text{H}_2$  units have been assembled to produce a  $\text{C}_6\text{H}_6$  ligand.

## Perspectives

A number of new applications have been designed that make use of the general NRMS idea and hold great promise for the future. New instruments have been developed;<sup>40</sup> one device relies on quadrupolar mass filters for the ion selection and analysis, which significantly reduces the cost of the experimental arrangement,<sup>40a</sup> and this setup has also been used to develop new scan techniques<sup>41a,b</sup> and time-variable NRMS experiments.<sup>41c</sup> This approach has indeed been shown to yield further information on the neutrals' unimolecular chemistry. McLafferty and co-workers<sup>42</sup> have demonstrated that not only may stationary gases be used for the neutralization process but also neutral species can be produced from high-energetic ion beams through surface collision. There is still a considerable effort in trying to understand the physical background of the electron-transfer processes, and studies have been carried out aimed at understanding the different energetic features of the ion beam at higher scattering angles.<sup>43</sup> Further insight into these phenomena is in fact desirable in order to obtain a clearer picture of the electronic situation governing the experiments. Another approach has been the implementation of the NRMS technique for analytical purposes, and in principle the method may serve for the quantitative analysis of isomeric mixtures<sup>44</sup> and the differentiation of stereoisomers<sup>41b</sup> as well as the monitoring of selected species in mixtures.<sup>41a</sup>

However, we hope to have convinced the reader that Fred McLafferty's statement, "NRMS has made its largest contribution to research areas outside mass spectrometry in the characterization of reactive or unstable molecular and radical species",<sup>4d</sup> certainly holds true; "Pandora's box", as he worded it, is still open and—in our view—contains better things than evil.<sup>45</sup>

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(45) While the term "Pandora's box" usually has a negative connotation, this view is misleading in that it is the historical result of a cultural misconception. For a superb discussion of this intriguing topic, see: Panofsky, D.; Panofsky, E. *Die Büchse der Pandora: Bedeutungswandel eines mythischen Symbols*; Campus: Frankfurt/New York, 1992.