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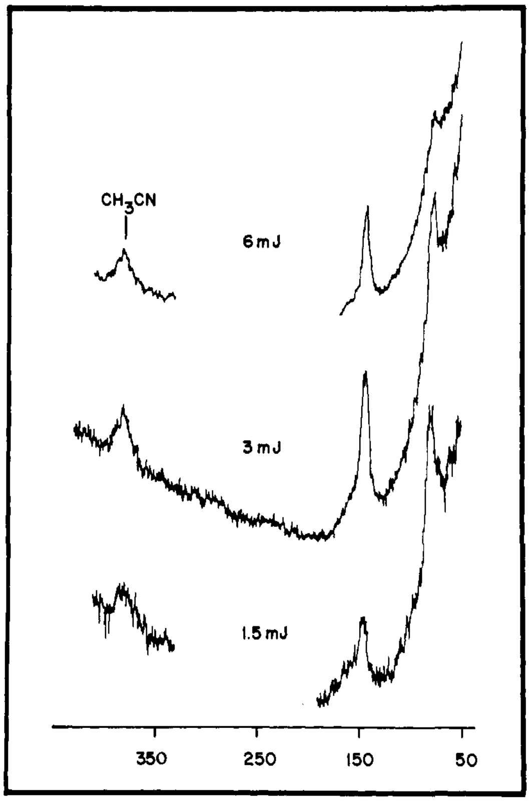

Figure 2. Dependence of the pulse-excited (531.8 nm, 7 ns pulses) spectrum of $Rh_2b_4^{2+}$ upon per pulse laser energy. Note that the intensity of the ground-state metal–metal stretching mode (79 cm^{-1}) diminishes relative to the excited-state metal–metal stretch (144 cm^{-1}) with increasing per pulse energy, therefore with increasing excited-state saturation. Pulse energy: lower trace, 1.5 mJ; middle trace, 3.0 mJ; upper trace, 6.0 mJ.

fluorescence (656 nm). These features have been assigned to allowed transitions of the $E_u(^3A_{2u})$ state ($\tau \sim 8.5$ μs) involving distortion along the Rh–Rh coordinate. Excitation at 531.8 nm, where these transitions have considerable absorption intensity, is expected to result in large resonance Raman intensity enhancements of the Rh–Rh stretching vibration.

The singlet ($^1A_{2u}$) lifetime was determined to be less than ~2 ns, and the quantum yield for intersystem crossing was found to be large [Φ(isc) ~ 0.8]. Thus, during our 7-ns Nd:YAG laser pulse, the major species present is the $E_u(^3A_{2u})$ state of $Rh_2b_4^{2+}$. Decay of this excited state to the ground state is complete in the 100 ms between laser pulses.

The $^1A_{1g}$ and $E_u(^3A_{2u})$ resonance Raman spectra of $Rh_2B_4^{2+}$ are shown in Figure 1. The ground-state spectrum (lower trace) shows an intense peak at 79 cm^{-1} with two overtones and a weak feature at 467 cm^{-1}. The 79-cm^{-1} band is clearly attributable to the Rh–Rh stretching motion, on the basis of its huge resonance enhancement [~10^5 times (mol/mol) the acetonitrile intensity] and depolarization ratio of ~$^1/_3$. The 467-cm^{-1} band is assigned to the Rh–C stretch. It shows a smaller resonance enhancement, which is consistent with its assignment as a vibration orthogonal to the Rh–Rh axis.

The upper curve of Figure 1 shows the excited-state TR^3 spectrum of the same solution of $Rh_2b_4^{2+}$. The principal feature of this spectrum is the intense band at 144 cm^{-1}, with an overtone at ~284 cm^{-1} and a weaker peak at 484 cm^{-1}. The 144-cm^{-1} feature is attributable to the excited-state Rh–Rh stretch (vide infra), and the 484 cm^{-1} band is assigned as the excited-state Rh–C stretch. This TR^3 spectrum is independent of the $Rh_2b_4^{2+}$ counterion (ClO_4^-, BPh_4^-, $CF_3SO_3^-$), and it is also independent of the solvent (CH_3CN, DMF).

The TR^3 spectra of $Rh_2b_4^{2+}$ as a function of per pulse laser energy at 531.8 nm (Figure 2) confirm the assignment of the 144-cm^{-1} vibration as the excited-state Rh–Rh stretch. When the incident per pulse laser energy was varied from 1.5 to 6 mJ/pulse, the 144-cm^{-1} peak increased in intensity as the 79-cm^{-1} intensity decreased. This observation is independent of the order in which the spectra were taken and is entirely reversible, clearly correlating the 79- ($^1A_{1g}$) and 144-cm^{-1} [$E_u(^3A_{2u})$] vibrational modes.

The observed increase in the Rh–Rh stretching frequency from 79 ($^1A_{1g}$) to 144 cm^{-1} [$E_u(^3A_{2u})$] corresponds to *greater than a* factor *of 3* increase in the restoring force for this normal mode in the excited state. Owing to ligand contributions in this mode, the increase in the force constant of the Rh–Rh bond itself must be even greater.[15] The large increase in the Rh–Rh stretching force constant clearly establishes that the Rh–Rh bond order is much higher in $E_u(^3A_{2u})$ than in $^1A_{1g}$, as predicted. An estimate of 42 kcal/mol for the Rh–Rh bond energy in $E_u(^3A_{2u})$ has been obtained[9] from an analysis of the vibronic structure of the $E_u(^3A_{2u}) \leftarrow {}^1A_{1g}$ system in the absorption spectrum of $Rh_2b_4^{2+}$. The 42 kcal/mol estimate is substantially larger than the 18 kcal/mol upper limit placed[9] on the Rh–Rh bond energy in the ground state of $Rh_2b_4^{2+}$.

The Rh–Rh bond order will clearly decrease when $E_u(^3A_{2u})$ is quenched by electron transfer, whether the excited state gains an electron (in the $4d_{z^2}\sigma^*$ orbital) or loses an electron (from the $5p_z\sigma$ orbital). The Rh–Rh force constant change need not be the same, however, for reductive and oxidative quenching, because the $4d_{z^2}\sigma^*$ and $5p_z\sigma$ contributions to the force constant may differ considerably. These contributions are crucial because they control the Franck–Condon barriers associated with electron transfer to and from the $E_u(^3A_{2u})$ state as well as those for the electron back transfers of the $Rh_2b_4^+$ and $Rh_2b_4^{3+}$ product ions. Studies aimed at elucidating these points are in progress in our laboratories.

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(15) TR^3 spectroscopic measurements on $Rh_2(CNPh)_8^{2+}$ in CH_3CN solution yield 162 cm^{-1} for the Rh–Rh stretching frequency in the triplet state of this related unbridged complex. Here the increase in the Rh–Rh frequency over the ground-state value (60 cm^{-1}) is even more dramatic, apprently reflecting negligible mixing of ligand modes and the Rh–C deformation with the Rh–Rh stretching coordinate. The Rh–Rh force constant is roughly 7.3 times greater in $E_u(^3A_{2u})$ than in the grond state of $Rh_2(CNPh)_8^{2+}$.

Thermal Desorption of Quaternary Ammonium Cations

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Quaternary ammonium salts are a challenge to the mass spectroscopist, both becasue they are difficult to analyze due to their nonvolatility and because a number of biologically important compounds (e.g., acetylcholine, choline chloride) are quaternary salts.[1] Attempts to volatilize quaternary ammonium salts prior to either electron ionization or chemical ionization (EI or CI) generally results in degradation to a neutral tertiary amine by loss of HX or RX (R = organic radical, X = halide). Ionization then produces R_3N^+ (EI) or R_3NH^+ (CI) and the appropriate fragments, from which the structure of the parent cation may be deduced.[2]

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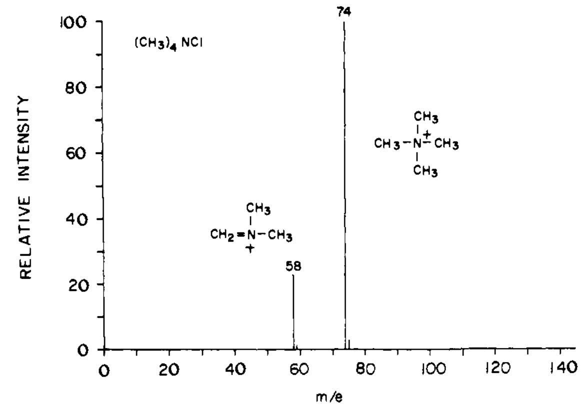

Figure 1. Thermal desorption mass spectrum of tetramethylammonium chloride. Heater current is 1.8 A. The heater is at ground potential.

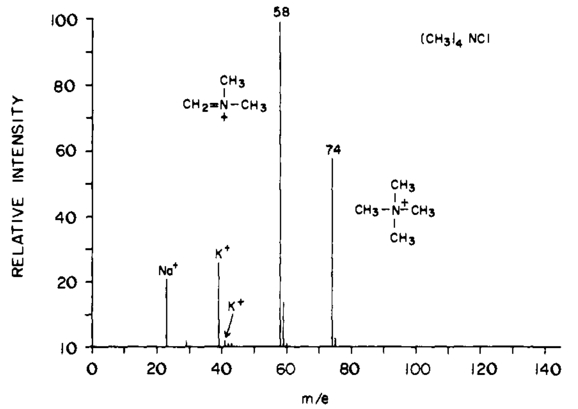

Figure 2. Thermal desorption mass spectrum of tetramethylammonium chloride. Heater current is 3.0 A. The heater is at ground potential.

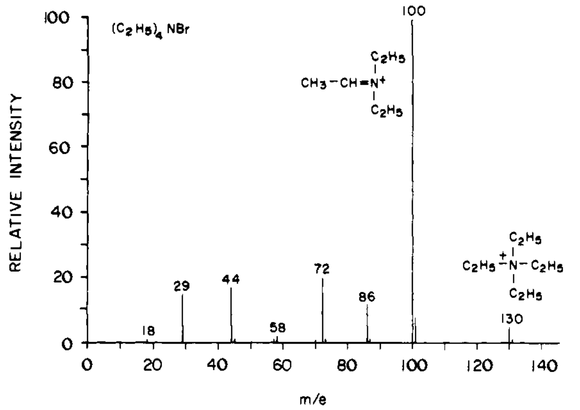

Figure 3. Thermal desorption mass spectrum of tetraethylammonium bromide. Heater current is 2.0 A. The heater is biased at +15 V with respect to the source block.

Intact cations from quaternary ammonium salts have been observed by a number of investigators using more exotic ionization techniques, including field desorption (FD) with untreated emitter wires[3] to obtain $(R_4N)_2X^+$ as well as R_4N^+, flash volatilization followed by EI to produce R_4N^+ (ions were not observed in the absence of the electon beam),[4] and a continuous wave CO_2 laser, where R_4N^+ ions were thought to be produced by multiphoton absorption.[5]

We report in this correspondence the production of R_4N^+ ions from quaternary ammonium salts by a process that is exclusively and unambiguously thermal, requiring no electron beams, electrostatic fields, or photons! The salts are deposited on a wire that is heated inside the ion source, and the R_4N^+ ions are desorbed and observed at temperatures below those necessary for the production of K^+ and Na^+. This work was done by using a Finnegan 4021 quadrupole mass spectrometer and a probe specially designed for thermal ionization. The important aspects of this instrumental configuration are that the probe, from which the samples are desorbed, is located inside the ion source at the point at which ions are normally made and extracted in the electron impact mode and the probe inlet is coaxial with the ion beam exit aperature. The probe itself is described elsewhere in detail.[6] The quaternary ammonium salts were dissolved in water or water/methanol, deposited on the filament, dried under a heating lamp, and then inserted into the ion source. Ions were obtained by passing a current of 1–4 A through the rhenium filament, which was generally biased at +15 V relative to the grounded ion source block. This voltage improved the extraction efficiency but had little effect on the spectra produced, since ions could be observed when the filament was at the same potential as the source block. Spectra could generally be observed for several minutes. Variation of filament current (temperature) resulted in changes in the observed spectra, with lower temperatures generally promoting production of the R_4N^+ ion and higher temperatures promoting the production of decomposition products and Na^+ and K^+ ions from the solvent. While the experimental configuration does not currently permit direct measurement of the filament temperature, reflected light from the filament, viewed through a window on the vacuum chamber, indicated that temperatures ranging roughly from 700, to 1000 °C were being employed in the experiments. Spectra were recorded by using a Finnegan/INCOS data system scanning at 2-s intervals.

The thermal desorption spectrum of tetramethylammonium chloride, $(CH_3)_4NCl$, is shown in Figures 1 and 2 at two different heater currents, 1.8 and 3.0 A, respectively. The R_4N^+ ion, *m/e* 74, appears as the base peak of the spectrum in Figure 1. The ions at *m/e* 58 and 42 are probably the result of pyrolysis on the filament, followed by desorption to give quaternary ions of the sort $CH_2{=}N^+(CH_3)_2$ and $CH_2{=}N^+{=}CH_2$, with the associated loss of one or two molecules of methane. It can be seen that the intensity of these increases with filament temperature. It is interesting to note that the favored fragmentations for this low-energy thermal process are the production of even electron ions and their corresponding neutrals. The ion appearing at *m/e* 30 is also an even electron species characteristic of the mass spectra of amines and probably corresponds to $CH_2{=}N^+H_2$. By contrast, the ions at *m/e* 59 and 43 most likely results from another decomposition pathway, that is the desorption of $(CH_3)_4N^+$ and $CH_2{=}N^+(CH_3)_2$, followed by the loss of the methyl radical. The intensity of the *m/e* 59 in particular is too great to be an isotopic satellite of *m/e* 58.

The mass spectrum of tetraethylammonium bromide is shown in Figure 3 and shows a pattern similar to $(CH_3)_4NCl$. The intact cation, $(C_2H_5)_4N^+$, appears at *m/e* 130. Loss of a neutral C_2H_6 and desorption of $(C_2H_5)_2N^+{=}CHCH_3$ appears at *m/e* 100. Unlike the tetramethyl case, however, the loss of two neutral ethane molecules to give a peak at *m/e* 70 is not the dominant process. Instead, successive losses of neutral ethylene groups produce the peaks observed at *m/e* 72 and 44.[7]

The mechanism producing the principal ions in this study is almost certainly s simple, direct temperature-dependent desorption or a simple pyrolysis followed by desorption. Fragmentation after desorption is minimal, since little excess energy is retained by the gaseous ions, and the major chemical reactions (losses of neutral species from tetravalent nitrogen cations) take place on the surface prior to desorption. An interesting experiment involves the examination of possible surface reactions between components in

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Table I. Ions Observed in the Thermal Desorption of a Mixture of Tetramethyl- and Tetraethylammonium Iodide Salts

m/e	species	relative abundance, %
	Intact Cations	
130	$(C_2H_5)_4N^+$	9.0
116	$(C_2H_5)_3N^+CH_3$	0.9
102	$(C_2H_5)_2N^+(CH_3)_2$	0.6
88	$C_2H_5N^+(CH_3)_3$	0.7
74	$(CH_3)_4N^+$	48.4
	Major Decomposition Ions	
100	$(C_2H_5)_2\text{-}N^+{=}C_2H_4$	95.0
86	$C_2H_5(CH_3)N^+{=}CH\text{-}CH_3$ $(C_2H_5)_2N^+{=}CH_2$	40.0
72	$C_2H_5(H)N^+{=}CH\text{-}CH_3$ $C_2H_5(CH_3)N^+{=}CH_2$	17.7
58	$(CH_3)_2N^+{=}CH_2$	100.0

a mixture of quaternary ammonium salts. Table I shows a portion of the spectra obtained by heating a filament coated with a solution containing approximately equal amounts of tetramethyl- and tetraethylammonium iodide. The major ions observed from this filament are the same as those shown in Figures 1–3 and are the result of the direct desorption or pyrolysis–desorption process. There are, however, a number of low-intensity ions that may be the result of a dequaternization/quaternization process of the sort described by Vincze and Gefon.[8] While interesting, the process is not a major one, which will be a distinct advantage in the analysis of mixtures or quaternary ammonium salts.

The temperatures at which the R_4N^+ ions desorb are lower than those at which K^+ or Na^+ are observed, as shown in Figures 1 and 2. While the Langmuir–Saha equation might be used to predict this observation, its use in this fashion is not strictly correct, since it predicts the ratio of desorbed ions to desorbed neutrals. Rather the process is more realistically expressed as (for sodium ions)

$$Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g)$$

and involves ionic bond rupture rather than ionization. The energy required for this process is the lattice energy, defined by

$$U_{\text{lattice}} = \Delta H_f(Na^+, g) + \Delta H_f(Cl^-, g) - \Delta H_f(NaCl, s)$$

If standard heats of formation for gaseous ions[9] and crystalline NaCl are used,[10] the process for thermal desorption of Na^+ and Cl^- requires an energy of 184 kcal/mol (8.0 eV). For KCl, using similar tables, the energy required is 167 kcal/mol (7.2 eV). Heats of formation for $(CH_3)_4N^+$ and lattice energies for $(CH_3)_4NCl$ are not available, but one may place an upper limit on this value by considering the lattice energy of NH_4Cl, reported as 153 kcal/mol (6.6 eV).[11] Since substitution of methyl groups to form $(CH_3)_4NCl$ would increase the ionic radius of the cation, increase the ionic bond length, and decrease the ionic strength, the production of $(CH_3)_4N^+$ through bond rupture would be expected to require somewhat less energy than the production of NH_4^+. While use of crystal lattice energies and heats of formation in a Born–Haber cycle, where the actual physical states of the species on a heated surface are not completely known, may not be completely justified, the general scheme substantiates the observation of quaternary ions at lower temperatures than potassium and sodium ions. Röllgen[3] has observed a related phenomenon in FD, in which desorption of quaternary ammonium ions and alkali attachment to polar molecules both occur at lower field strengths than the field ionization of molecules having low ionization potentials.

It is generally expected that heating quaternary ammonium salts in the vacuum region of a mass spectrometer results in a decomposition process in which losses of alkyl groups produces tertiary amines which are volatilized as *neutrals* prior to ionization by electron impact or chemical ionization. This major thermal process occurs in this study as well but is not observable with the electron beam off. Rather, only those reactions, which produce stable ionic products retaining a tetravalent nitrogen, result in desorption of *ions*, which can be observed without an electron beam, when formed inside the ion source. Stoll and Röllgen have also recently reported the thermal desorption of quaternary ammonium ions[12] but, unlike this present work, have not observed the surface reactions leading to the desorption of stable cationic fragments.

Not only does this study demonstrate the ability to desorb stable cations of organic compounds without the aid of auxiliary ionization techniques, but it also demonstrates a method by which these and related materials may be ionized by using rather standard mass spectrometry instrumentation. Because electrostatic fields are unnecessary, it is likely that anions are produced simultaneously with the cations, so that organic anions might also be subject to analysis by this simple process. Finally, this work suggests the role of thermal processes in other ionization techniques, such as laser, field, and plasma desorption, and as such represents an important contribution to the understanding of these mechanisms.

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A Novel Photoreaction of Thymidine with Lysine. Photoinduced Migration of Thymine from DNA to Lysine[1]

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Cross-linking of proteins to DNA is one of the important processes that can take place when bacterial or mammalian cells are irradiated with UV light.[2] Investigation of this type of cross-linking is particularly useful in understanding the nature of radiation-induced damage in cells.[2] Direct photocross-linking technique, without the aid of other reagents, also provides an important method for studying specific protein–nucleic acid associations.[3] Knowledge of the photoreactions of relevant model systems could be of significant value in achieving an understanding of UV-induced cross-links.[4] Shetlar and co-workers recently reported that irradiation of thymine-labeled DNA and lysine in aqueous solvent followed by acid hydrolysis produces a photoproduct that behaves like thymine–lysine adduct,[5] while the

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