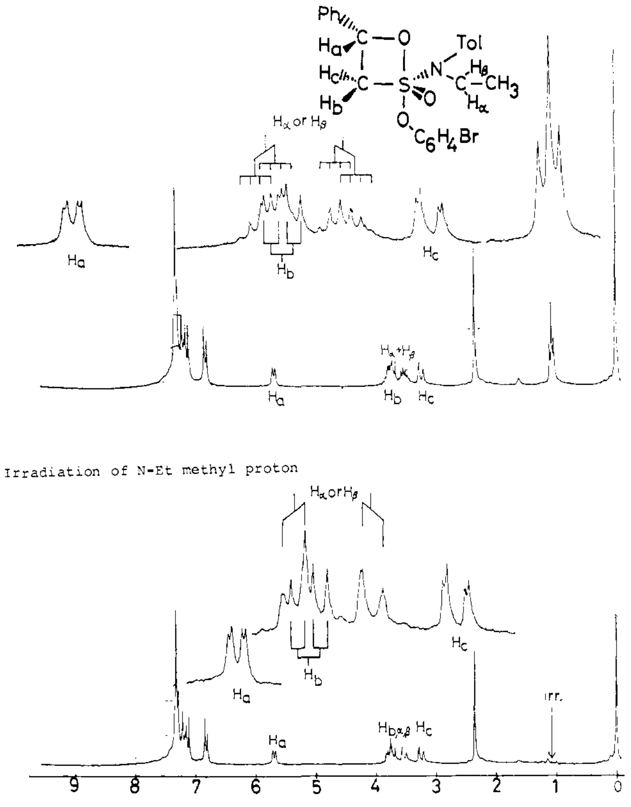
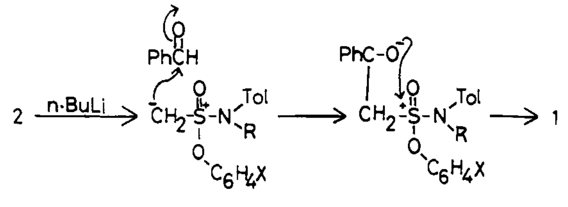


Figure 2. 200-MHz ^{1}H NMR spectra of compound **1b**.

forming unusual four-membered cyclic compounds resembling the intermediates of the Wittig reaction.



Gassman and Amick found that the reaction of aryloxysulfonium salts with bases at low temperature gave ortho-substituted phenols via [2,3]-sigmatropic rearrangement.[8] We recently synthesized diaminooxosulfonium salts by alkylation of the corresponding sulfoximines.[9] Their reaction with dimsylsodium gave the corresponding ylides, whose negatively charged parts rearranged to the ortho positions of the arylamino substituents to give dihydrobenzoisothiazole derivatives. On the other hand, Johnson and Rogers reported that the reaction of aminooxosulfonium ylides with carbonyl compounds in presence of bases yielded the corresponding epoxides and sulfinamides.[10] The present result differs entirely from the results cited above. We could thus find a new reaction pathway of oxosulfonium ylides.

According to Martin et al., the incorporation of the sulfurane function into a five-membered heterocyclic ring has a dramatic effect on its rates of reaction (reactivity order: acyclic, monocyclic, spirobicyclic).[11] We examined the reaction of **2d** with sodium phenoxide, intending to obtain an acyclic sulfurane oxide. Treatment of **2d** with sodium phenoxide afforded not an expected sulfurane oxide but only a mixture of decomposition products. And sulfurane oxide was not obtained by the benzaldehyde reaction of **2d**. The above results suggest that an acyclic aminodioxysulfurane oxide is ordinarily unstable, and a halogeno group in an aryloxy substituent is necessary to stabilize a sulfurane oxide. An additional factor in the stability of **1** might be the interaction between the lone pair of electrons of the nitrogen with the sulfurane oxide function. Law and Martin found evidence for such interaction between the sulfurane oxide functional group and the lone pair on carbon of an anion derives by the deprotonation of a methyl group attached to sulfur.

In summary, we have shown that aminodioxysulfurane oxides **1** were prepared by the reaction of aminoaryloxyoxosulfonium ylides with benzaldehyde via intramolecular addition of corresponding betaines. Although the general applicability of our results remains to be proved, it is clear that this is the first reaction pathway of oxosulfonium ylides to sulfurane oxides.

We are currently investigating the exact structure of **1** in greater detail.

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(12) Satisfactory values of elemental analysis were obtained for new compounds except for **2a** and **2d**. Compound **2a** is a glassy substance, and **2d** is easily decomposed. M.p.: **2b**, 122–123; **2c**, 117–119; **2d**, 116–117 dec; **3a**, 76–77; **3b**, 90–91; **3c**, 101–102 °C.

Vibronic Spectra of Naphthalene and Naphthalene-d_8 Cations in Solid Argon

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There has been considerable recent research on optical spectroscopy of molecular cations in noble gas matrices. These studies have involved both stable and photosensitive cations such as hexafluorobenzene,[1] other fluorine-substituted benzene cations,[2] and diacetylene cation[3] on one hand and toluene[4] cycloheptatriene,[5] halotoluene,[6] and styrene cations[7] on the other. Naphthalene has been studied extensively by photoelectron spectroscopy,[8-11] and the absorption spectrum of naphthalene cation (hereafter N$^+$) has been observed in a variety of glassy matrices.[12-14] The absorption spectrum of N$^+$ in noble gas matrices provides both vibrational and electronic data, which may be compared to photoelectron spectra in order to better understand the ion itself and the ion-matrix interaction.

The cryogenic apparatus and photoionization source have been described previously.[15,16] After suitable outgassing, naphthalene

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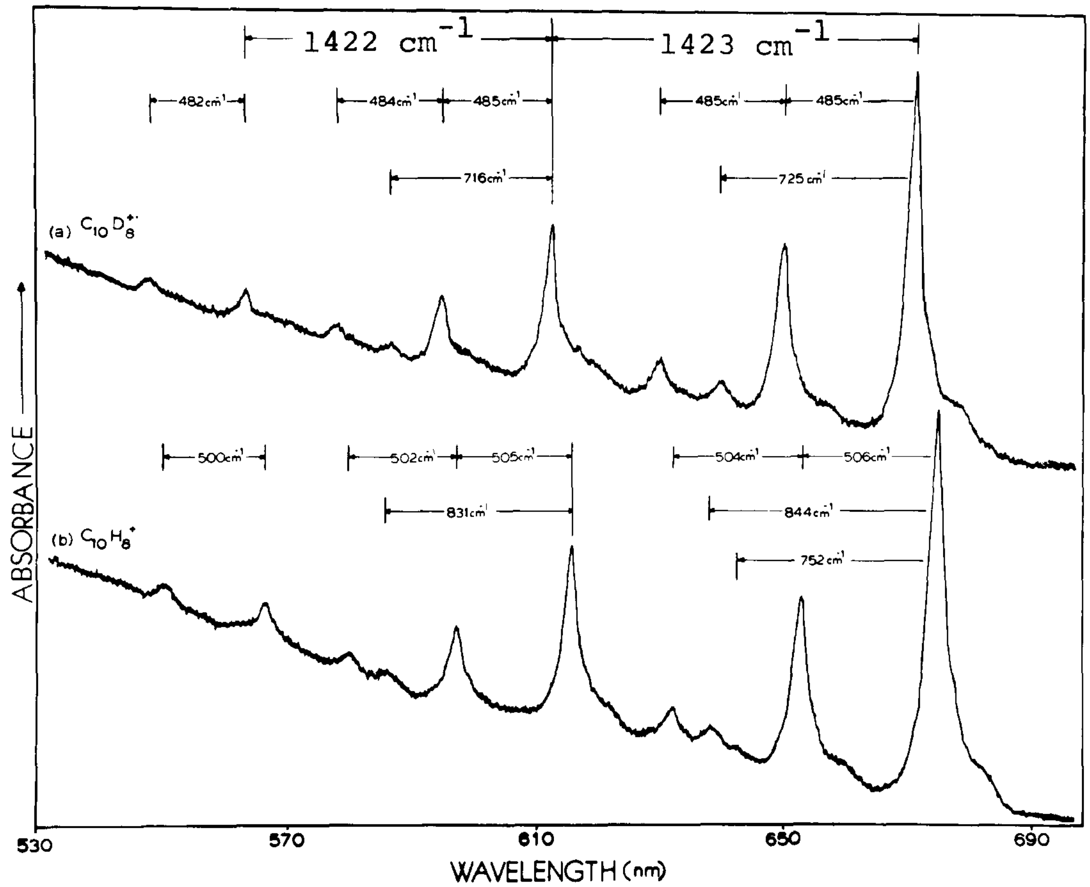

Figure 1. Absorption spectra in the red region following argon matrix photoionization of naphthalene vapor during condensation with excess argon at 18 ± 2 K for 4 h. (a) $C_{10}D_{18}$; (b) $C_{10}H_8$.

was sublimed through a needle valve (20 °C) onto the sapphire window (18 ± 2 K) along with argon flowing through a 3-mm orifice discharge tube (1 mM/h). Spectra recorded on a Cary 17 spectrophotometer revealed a strong precursor absorption at 272 nm and an estimated naphthalene concentration of 1% with the sample needle valve opened two turns.

Three experiments were performed with the flowing argon excited by microwave discharge using 75% power with a standard diathermy unit. With the needle valve opened one, two, and five turns for successive 1-h periods of deposition, sharp product absorption was found at 675 nm with the first two settings, but five turns admitted excessive precursor for product isolation. The spectrum from a second experiment with the needle valve open two turns is illustrated in Figure 1b; a strong vibronic absorption was observed beginning at 675.2 ± 0.1 nm ($A = 0.11$) and weaker bands were observed at 461 nm ($A = 0.005$) and 381 nm ($A = 0.03$). Photolysis with 500–1000-nm radiation for 30 min reduced these bands approximately 10%; a like exposure to 220–1000-nm radiation reduced these bands another 60%. A third experiment using 1 turn on the needle valve and codeposition with argon discharge radiation for 6 h produced sharper spectra; the 675.2-nm band ($A = 0.17$) was 60-cm^{-1} wide at half-maximum. Using krypton as the discharge and matrix gas shifted the origin to 679.5 ± 0.1 nm (110-cm^{-1} half-width); the vibrational intervals were unchanged. Two experiments performed with $C_{10}D_8$ produced a strong red system beginning at 671.8 ± 0.1 nm ($A = 0.20$) (Figure 1a) and weaker bands at 458 ($A = 0.008$) and 379 nm ($A = 0.04$).

The vibronic band system beginning at 675.2 nm and the weaker bands at 461 and 381 nm are assigned to N^+ owing to their agreement with N^+ bands at 709, 488, and 395 nm in butyl chloride glass,[12] similar bands at 694, 472, and 391 nm in a Freon glass,[13] and energy differences between photoelectron (PES) band maxima which predict absorptions at 670, 457, and 376 nm. Argon resonance radiation (11.6 eV) from the discharge photoionizes naphthalene molecules (IE = 8.15 eV) which are subsequently trapped in the freezing argon matrix. The decrease in N^+ absorption upon sample photolysis is probably due to photodetachment from anion electron traps with subsequent neutralization of N^+.

The red absorption provides an excellent basis for comparison between PES and the sharp matrix absorption spectrum since sharp vertical PES band origins (± 0.01 eV) were observed for the first and third ionic states of N^+. The PES band difference is 1.85 ± 0.02 eV[11] which predicts an absorption origin at 14 920 ± 160 cm^{-1} in the gas phase, assuming no change in structure between the neutral molecule and the two ionic states. The argon matrix origin at 14 810 ± 3 cm^{-1} is in agreement within measurement error, which indicates relatively little perturbation of N^+ by the argon matrix. This assertion is supported by the small shift of the origin 93 cm^{-1} to lower energy in solid krypton and the lack of a measurable change in the vibrational intervals.

The vibronic structure (Figure 1) is also of interest for comparison to the neutral molecule and structure in the PES. The major interval in the N^+ spectrum, 1422 ± 6 cm^{-1}, was unchanged upon deuterium substitution. This is in agreement with the 1420 ± 20-cm^{-1} interval in the first PES band,[8,11] which is probably due to the C(9)–C(10) stretching mode $\nu_4(a_g)$. The second repeated interval in the spectra was approximately 505 cm^{-1} for N-h_8^+ and 485 cm^{-1} for N-d_8^+; this corresponds to the $\nu_9(a_g)$ skeletal distortion observed in the Raman spectra for N-h_8 at 512 cm^{-1} and N-d_8 at 491 cm^{-1}.[17] The 752-cm^{-1} interval corresponds to $\nu_8(a_g)$, the skeletal breathing mode observed at 758 cm^{-1} in the Raman spectrum. Totally symmetric (a_g) vibrational modes are active in this long-axis-polarized, dipole-allowed $^2B_{2g} \leftarrow {}^2A_u$

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transition. Weaker bands separated by 844 cm^{-1} (and 831 cm^{-1}) with deuterium counterparts near 720 cm^{-1} correspond, however, to the out-of-plane C–H bending mode at 874 cm^{-1} (deuterium counterpart 752 cm^{-1}). This b_{3g} mode is vibronically allowed with z-polarized radiation.

The much weaker band at 461 nm in solid argon can be assigned to the short-axis-polarized, dipole-allowed $^2B_{3g} \leftarrow {}^2A_u$ transition based upon $^2B_{3g}$ idenification[10] of the fourth PES band. The dipole change along the long axis is much greater than along the short axis as shown by the relative intensities of the 675- and 461 -nm N$^+$ absorptions. The 381-nm absorption, corresponding to an 11.4-eV PES peak,[10] is probably due to an allowed $\sigma \leftarrow \pi$ transition.

Comparison of vibrational intervals in the third photoelectron band and the structured matrix absorption is complicated by the 250-cm^{-1} PES bandwidth. The first three vibronic peaks are separated by 500 ± 20 cm^{-1}, in agreement with the matrix spectrum; the fourth vibronic peak is broadened and probably contains some 1420-cm^{-1} and (3 × 500)-cm^{-1} vibrational spacing.

For large rigid molecular cations like N$^+$ with relatively low electron affinities (8.15 eV) compared to the ionization energy of argon (15.8 eV), the argon matrix–cation interaction is minimal, as shown by comparison of the electronic band origin with the PES. The observed vibrational intervals show little change from fundamentals for the neutral molecule; this contrasts the case of smaller parent molecular ions like CH$_2$F$_2^+$ where the hole has a greater effect on the vibrational potential function of the molecule.[18]

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High-Resolution NMR Spectra of Quadrupole Nuclei in Solution Using Multiple Quantum Coherence

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The utilization of multiple quantum coherence (MQC) in NMR experiments probing molecular structure and dynamics is becoming increasingly common. The principal attraction has been the simplification of both spectra and spin relaxation mechanisms that results from the reduced number of MQ transitions between energy levels. To date, MQC experiments have been performed on quadrupole nuclei in ordered systems,[1,2] dipolar coupled spin-$^1/_2$ nuclei in ordered systems,[3-6] and scalar coupled spin-$^1/_2$ nuclei in solution.[7-10] These experiments have in many cases yielded structural and dynamic information inaccessible via one quantum spectra alone.

A relatively unexplored area of MQC applications is that of quadrupole nuclei in solution. Quadrupole nuclei are subject to the same chemical shieldings and scalar couplings which are valuable structural parameters for spin-$^1/_2$ nuclei. These parameters are, however, obscured by the broad lines and resultant poor resolution usually found in spectra of quadrupole nuclei. MQC offers a possibility for improvement of resolution in that both chemical shifts and splittings due to spin–spin coupling scale as the number of quanta involved, while line widths due to quadrupole broadening can remain independent of or actually decrease with number of quanta. Development of techniques for observation of MQC of quadrupole nuclei in solution is, therefore, worthy of exploration.

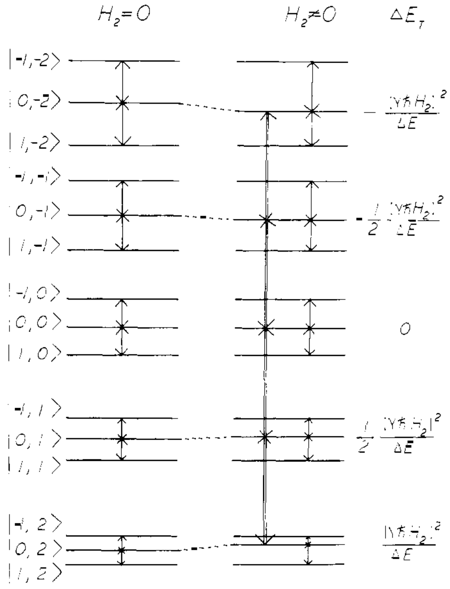

Figure 1. $^{14}NH_4^+$ energy level diagram showing the effect of spin tickling. ^1H spin tickling is applied at the central line of the ^1H triplet as shown by the double arrows. Single arrows show the 1Q transitions. Spin states are indicated by Z-magnetization quantum numbers for ^{14}N states and total ^1H states. The energy changes ΔE_T due to spin tickling, listed to the right of the figure, were calculated from second-order perturbation theory using $H' = \gamma\hbar H_2 I_x$, where γ is the gyromagnetic ratio, H_2 is the tickling field, and I_x is the x component of the spin operator.

Unfortunately, direct application of commonly used pulse sequences does not result in observable MQC for most quadrupole nuclei in solution. This arises because of the degeneracy of one quantum (1Q) transitions and necessitates explicit modification of experimental procedures. We present here one option which proves successful in observing MQC for spin-1 nuclei which show some residual spin–spin coupling. This option employs removal of degeneracy by spin tickling. We will illustrate use of this method on ^{14}N spectra of NH$_4$Cl in aqueous solution.

MQC spectra are commonly observed by using the pulse sequence 90°-τ-90°-t_1-90°-t_2 in which 90° represents rf pulses of sufficient length to rotate magnetization by 90° in the rotating frame and τ, t_1, and t_2 represent time delays.[6,7,10] The effect of this sequence is best seen by employing density matrix methods. For the $^{14}NH_4^+$ case, each ^{14}N line associated with a particular ^1H spin state can be described by using a 3 × 3 matrix. One quantum coherence, represented by spin density matrix elements σ_{12} and σ_{23}, is excited by the first 90° pulse. Under favorable conditions, the 1Q elements evolve during τ such that their phases differ at the time of the second 90° pulse. The second pulse then mixes these density matrix elements to produce a finite MQC that evolves during t_1 according to MQ spectral parameters. The final 90° pulse mixes MQC back into 1Q density matrix elements which can be observed via their relationship to transverse magnetization during the time period t_2. The time period t_1 is incrementally increased over a period appropriate for decay of the MQC and the data transformed in the two dimensions, t_1 and t_2, to produce normal 1Q spectra in the F$_2$ dimension and MQC spectra in the F$_1$ dimension.

The reason this sequence is ineffective for a spin-1 nucleus in solution can best be illustrated following a treatment given by

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