not very great. We note also in passing that the popular combination rules for Lennard-Jones parameters

$$\sigma = \frac{1}{2}(\sigma_1 + \sigma_2),$$

$$\epsilon = (\epsilon_1 \epsilon_2)^{\frac{1}{2}},$$

even with the modification which is necessary for dipole molecules² does not reproduce the shifts.

A fuller account of these computations will be published in the Journal of Quantitative Spectroscopy and Radiative Transfer.

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Long-Range N¹⁴ Coupling in Ethyl Ammonium Ions

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THERE has been considerable interest recently in the magnitudes and relative signs of CH₃-X and CH₂-X coupling constants in compounds of the type (CH₃CH₂)_nX²⁻⁸. We wish to report the analysis of the spectra of N(CH₂CH₃)₄⁺ and N(C₂H₅)₃(CH₂SCH₃)⁺ and the confirmation of the assignments of these spectra by H¹-{N¹⁴}¹ double resonance and by the temperature dependence of the proton spectra.

The spectrum of the methyl protons of

in water solution at 40.0 Mc/sec is shown in Fig. 1. Additional structure on each of the peaks of the usual 1:3:1 triplet is quite apparent.⁹ The spectrum of the methylene protons is also shown in Fig. 1. The methylene proton spectrum consists of the expected 1:3:3:1

quartet with no additional structure. The main structure of these multiplets is readily assigned to coupling of the methyl and methylene protons with $J_{\text{CH}_2-\text{CH}_3} = 7.2$ cps. If it is assumed that the additional structure on the methyl peaks arises from coupling with the N¹⁴ nucleus (spin 1) with $J_{\text{N}-\text{CH}_3} = 1.8$ cps and $J_{\text{N}-\text{CH}_2} = 0.0$, the calculated spectrum shown in Fig. 1 is obtained. The observed spectrum is in good agreement with the spectrum calculated with the above values of the coupling constants.

The effect of H¹-{N¹⁴} double resonance on the methyl proton spectrum is also shown in Fig. 1. The application of a strong radio-frequency field at the N¹⁴ resonance frequency causes the collapse of the additional structure on the methyl resonance. The assignment of this structure to N¹⁴ coupling is thus confirmed. Double irradiation at the N¹⁴ resonance frequency has no effect on the methylene proton spectrum, indicating that $J_{\text{N}-\text{CH}_2}$ is less than 0.5 cps.

Further confirmation of the above analysis of the "extra" structure to the proton resonance of a CH₃ group which is part of an ethyl group attached to nitrogen is provided by studies of temperature dependence of this structure. The relaxation times for quadrupolar nuclei in nonspherically symmetrical electrical environments increase with increasing temperature.¹⁰ This effect for N¹⁴ is illustrated in the temperature dependence of the H¹ spectrum of CH₃ of the ethyl groups of N(C₂H₅)₃(CH₂SCH₃)⁺I⁻ (Fig. 2). Triplet structure arising from coupling between N¹⁴ and the methyl protons is washed out by rapid N¹⁴ quadrupolar relaxation at 28°C, but becomes just resolvable at 101°C.

FIG. 1. Single resonance proton spectra observed for the CH₂ and CH₃ groups in N(CH₂CH₃)₄⁺ Br⁻/H₂O at 40.0 Mc/sec and double resonance spectrum of the CH₃ group with strong irradiation at the N¹⁴ resonance frequency. Analysis gives $J_{\text{N}-\text{CH}_3} = 1.8$, $J_{\text{N}-\text{CH}_2} = 0.0$, $J_{\text{CH}_2-\text{CH}_3} = 7.2$, and $\delta_{\text{CH}_2-\text{CH}_3} = 81.4$ cps.

FIG. 2. Temperature dependence of the proton spectrum of the ethyl CH_3 groups of $\text{N}(\text{C}_2\text{H}_5)_3(\text{CH}_2\text{SCH}_3)^+\text{I}^-/\text{D}_2\text{O}$ at 60 Mc/sec.

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¹ The notation $\text{H}^1 - \{\text{N}^{14}\}$ indicates a double resonance experiment in which a strong radio-frequency field is applied close to the N^{14} resonance frequency while the proton spectrum is studied with a weak radio-frequency field.

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Addendum: Vibration-Rotation Spectra of BrCN

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RECENT measurements¹ of the infrared spectrum of BrCN have indicated that the value of α_3 might be larger for the heavier bromine isotope than for the lighter one. The vibration-rotation structure of the fundamental ν_3 has now been measured and the values obtained for α_3 are in excellent agreement with those found from the measurements reported in the earlier

TABLE I. Vibrational frequencies of BrCN.

Transition	Molecular species	$\nu_0(\text{cm}^{-1})$	$B' - B''(\text{cm}^{-1})$
001-000	Br^{79}CN	2198.29 ± 0.02	-0.000672 ± 0.000002
001-000	Br^{81}CN	2198.29 ± 0.02	-0.000684 ± 0.000002
01 ¹ 1-01 ⁰	Average of Br^{79}CN & Br^{81}CN	2192.10 ± 0.02	-0.00069 ± 0.00001
01 ⁰ 0-000	Br^{79}CN	341.67 ± 0.04	...
01 ⁰ 0-000	Br^{81}CN	341.61 ± 0.04	...

work.¹ The observation of the Q and a number of P and R lines of the first "hot band" make it possible to obtain a better value for the frequency of the bending fundamental (ν_2) by means of the Ritz principle.

The spectra were obtained using a liquid-nitrogen cooled PbSe detector and a 2000 lines per inch grating. The third order of the grating was used and a resolution of about 0.09 cm^{-1} was attained. Absorption lines of CO were superimposed on the spectrum for calibration. Lines with J values up to 57 were sufficiently well resolved and were measured, but higher J lines were too badly overlapped for measurement. The curves give no indication of a ΔD term, although a D'' of the magnitude given by Burrus and Gordy² is evident.

Table I gives the band centers and ΔB values observed in this work as well as the values of ν_2 obtained through application of the Ritz principle. Table II contains the values of the vibration-rotation constants which supplement or replace those given in reference 1. The limits of error given for the rotational constants in Table I were determined by standard deviations obtained from a least-squares analysis of the data. The standard deviation plus an additional estimate of the absolute accuracy were used to determine the limits of error given for the ν_0 's and for the constants given in Table II.

Taking the values of x_{22} , g_{22} , and α_2 it is possible to calculate the Fermi resonance constant W_{12} . The calculated value is $W_{12} = -33.3 \text{ cm}^{-1}$ for Br^{79}CN . While this value is not as close to the observed value of -35.41 as one would like, the agreement is better

TABLE II. Vibration-rotation constants for BrCN.

$\alpha_3(\text{Br}^{79}\text{CN}) = -0.000672 \pm 0.000003 \text{ cm}^{-1}$
$\alpha_3(\text{Br}^{81}\text{CN}) = -0.000683 \pm 0.000002 \text{ cm}^{-1}$
$x_{22} = -0.86 \pm 0.10 \text{ cm}^{-1}$
$x_{23} = -6.19 \pm 0.04 \text{ cm}^{-1}$
$g_{22} = 1.15 \pm 0.03 \text{ cm}^{-1}$
$\nu_1 + x_{13} = \begin{cases} 584.84 \pm 0.35 \text{ cm}^{-1} \text{ for } \text{Br}^{81}\text{CN} \\ 586.64 \pm 0.35 \text{ cm}^{-1} \text{ for } \text{Br}^{79}\text{CN} \end{cases}$
$W_{12}^{79} = -35.41 \text{ cm}^{-1}$
$W_{12}^{81} = -35.48 \text{ cm}^{-1}$