Letters to the Editor

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Communications

Raman Spectra and Vibrational Assignments for Trimethylamine

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Two recent articles[1,2] dealing with the vibrational assignments and normal coordinate analysis of trimethylamine are in disagreement on the disposition of certain fundamentals. In particular, on the basis of *P*- and *R*-branch separations, Gayles[1] reassigns a band at 1183 cm^{-1} to a degenerate methyl rocking mode and a band at about 1100 cm^{-1} to the a_1 methyl rocking mode. Dellepiane and Zerbi,[2] in their normal-coordinate treatment, have given arguments for the reverse assignment. New high-quality infrared spectra were presented,[1] but the only Raman data available are based on the spectrum of the liquid reported some time ago by Kohlrausch.[3] In connection with a recent study of

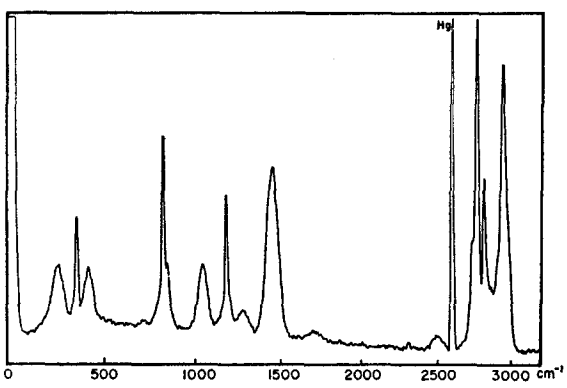

FIG. 1. Raman spectrum of gaseous $(CH_3)_3N$.

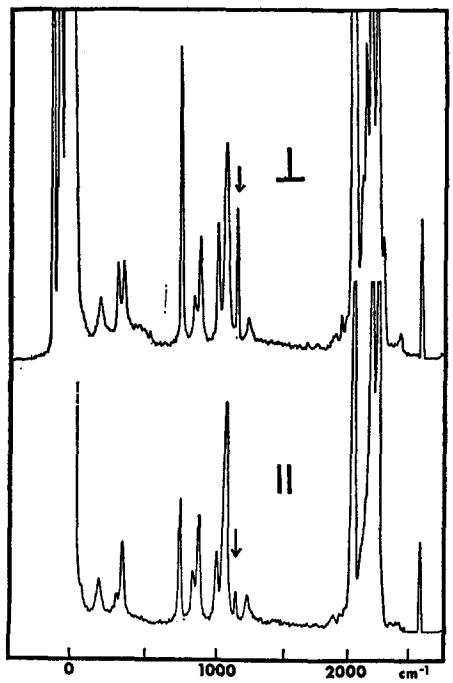

FIG. 2. Raman spectra of liquid $(CD_3)_3N$ at −10°C showing polarization properties.

trimethylamine complexes, we have had occasion to investigate the Raman spectrum of trimethylamine in the gas and liquid states as well as the spectra of the deuterated and ^{15}N isotopic species in the liquid. These new data, we believe, provide the necessary information to resolve the dispute

Theory predicts,[4] and experimental results have confirmed, that totally symmetric Raman bands of symmetric tops in gas-phase spectra are characterized by a strong intense *Q* branch with relatively weak rotational wings whereas degenerate bands are weaker and much more diffuse. These band shapes are quite characteristic for the identification of the symmetry species of a band.

In the Raman spectrum of gaseous trimethylamine shown in Fig. 1, one can immediately identify the three lowest a_1 fundamentals as the bands appearing at 364, 826, and 1183 cm^{-1}. All other bands appearing below 1300 cm^{-1} have band contours characteristic of degenerate modes. The band at 1102 cm^{-1} does not appear in the spectrum of the gas because of low intensity, but was observed as a depolarized line in the spectrum of the liquid. The Raman data thus agree with the assignments of Dellepiane and Zerbi.[2] With regard to the 1183-cm^{-1} band, despite its appearance as a parallel-type infrared band, Gayles states without elaboration that the *P*- and *R*-branch separation is compatible only with a band of *e* symmetry and a zeta constant of −0.2. However, the approximate formula of Gerhard and Dennison[5] which was used to calculate the *P*–*R* separations of the a_1 bands neglects vibration–rotation interactions, and this may account for the lack of agreement. Recent calculations for slightly asymmetric

TABLE I. Raman frequencies of trimethylamine (in cm^{-1}).[a]

$(CH_3)_3N$ Gas	$(CH_3)_3N$ Liquid	$(CD_3)_3N$ Liquid	Assignment
1485	1472 dp		$\nu_3\ \nu_{15}\ \nu_{16}$
1457	1448 dp	1068 dp	
1433	1420 ?	1008 p	$\nu_4\ \nu_{17}$
1283 br	1282 dp	1229 dp	ν_{18}
1183 sh	1191 p	1147 p	ν_5
...	1100 dp	840 dp	ν_{19}
1048 br	1048 dp	881 dp	ν_{20}
847 sh	...	...	$2\nu_{21}$
826 sh	833 p	748 p	ν_6
723 br			?
422 br	429 dp	357 dp	ν_{21}
364 sh	375 p	318 p	ν_7
266 br	277 dp	202 dp	ν_{22}

[a] sh=sharp, br=broad, p=polarized, dp=depolarized.

tops have shown that small changes in the upper-state rotational constants may have significant effects on the predicted band contours.[6]

No Raman spectra of deuterated species have appeared heretofore in the literature. Polarized spectra of liquid $(CD_3)_3N$ are shown in Fig. 2, and four of the five a_1 fundamentals below 1500 cm^{-1} can easily be identified. Of interest here is the fact that the weak infrared band at 1142 cm^{-1}, which was assigned by Gayles as a combination, actually is quite intense and polarized in the Raman effect (arrow) and therefore must be assigned to an a_1 fundamental. Frequencies for $(CD_3)_3N$ are listed in Table I. A normal coordinate analysis has been completed, and the full results, including the data for the ^{15}N species, will be published in the reasonably near future.

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Free Electrons in Liquid Hexane*

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Free electrons have recently been observed in rare-gas liquids[1] after suitable purification procedures, but in other liquids ions seem to have been the only stable charge carriers observed. Although arguments have been advanced[2] that the previously observed negative-charge carriers in saturated hydrocarbons were solvated electrons, there are several reasons to believe they were ions. First, the magnitude of observed mobilities were of the order of 10^{-3} $cm^2\ V^{-1}\cdot sec^{-1}$, very similar to the value for positive ions in the same liquids. Next, the mobilities were field independent up to 10^6 V cm^{-1}, a behavior characteristic of ions. Finally, the activation energy of the mobility of the negative species in liquid hexane is what one would predict by comparison with the rare gases by a law of corresponding states.[3] It seems very likely to us that the hydrocarbons studied had not been sufficiently purified of electron scavengers, oxygen, for example, to observe free-electron conduction.

It is the purpose of this Communication to report what we believe to be the first observations of electron charge carriers in liquid hexane. In highly purified hexane we have observed a mobility at least 50 times those previously observed in hexane. These charge carriers exhibit a field-dependent mobility at fields below 1000 V/cm and are strongly dependent on impurities. The fast charge carriers were observed only

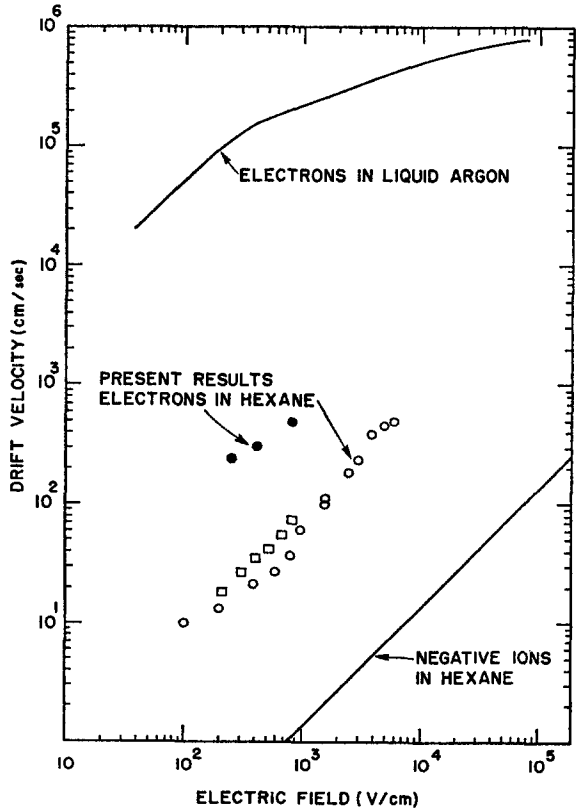

FIG. 1. Drift velocity versus electric field for free electrons in liquid hexane. The open and closed circles represent data obtained in a diode cell with hexane samples of different purity. The squares represent data obtained in an electronic double shutter cell[4] with a different hexane sample. The lower curve is for negative ions in liquid hexane from LeBlanc,[2] and the upper curve is for free electrons in liquid argon from Miller, Howe, and Spear.[1]