

should be regarded as approximate. The description probably gives the major contribution to the observed frequency.

The three C-H stretching fundamentals can easily be assigned to the bands around 3000 cm^{-1} . Each of these three frequencies for the carbon compound is higher than for the silicon compound, as is the case for all the vibrations except the *trans*-CH wag and CH_2 wag. The C=C stretch and CH_2 bend can be unambiguously assigned for both compounds. The in-plane bend of the lone hydrogen is expected around 1300 cm^{-1} and is assigned to the bands at 1306 (C) and $1283\text{ cm}^{-1}\text{ (Si)}$. The CH in-plane bend was observed at 1294 cm^{-1} for $\text{CH}_2=\text{CHCCl}_3$ ¹ and at 1266 cm^{-1} for $\text{CH}_2=\text{CHSiCl}_3$.²

The CF_3 stretches give rise to the bands in the $1100\text{--}1300\text{-cm}^{-1}$ region. There are two vapor-state bands in this region, at 1286 and 1173 cm^{-1} , but the 1173-cm^{-1} band is resolved into two bands in the solution spectrum. The SiF_3 group usually gives rise to two bands in the regions $980\text{--}945$ and $910\text{--}860\text{ cm}^{-1}$.³ The intense bands at 973 and 892 cm^{-1} can be assigned to these vibrations.

The CH_2 rocking frequency was assigned as 1129 cm^{-1} in $\text{CH}_2=\text{CHCCl}_3$,¹ but the only band that can be assigned to this vibration in $\text{CH}_2=\text{CHCF}_3$ was observed at 1024 cm^{-1} . There is a corresponding band observed at 1015 cm^{-1} in the silicon compound. This compound showed a weak band at 1153 cm^{-1} whose relative intensity changed with time and must be due to the formation of the Si-O-Si group, as stated by Shull, Thursack, and Birdsall for $\text{CH}_2=\text{CHSiCl}_3$.² These authors assigned the CH_2 rock of that compound to the band at 993 cm^{-1} , the CH_2 wag to 1008 cm^{-1} , and the *trans*-CH wag to 997 cm^{-1} , but Potts and Nyquist⁴ assigned the *trans*-CH wag and CH_2 wag for the same compound as 994 and 975 cm^{-1} , respectively, and the CH_2 rock can be assigned as 1008 cm^{-1} . The *trans*-CH wag and CH_2 wag of $\text{CH}_2=\text{CHCF}_3$ were assigned by Potts and Nyquist to bands at 979 and 965 cm^{-1} , but these were the only bands listed in their study. Our values are 980 and 964 cm^{-1} . In $\text{CH}_2=\text{CHSiF}_3$, the *trans*-CH wag is assigned to the band at 1006 cm^{-1} and the CH_2 wag as 977 cm^{-1} . The latter assignment is verified by the usual observation⁴ of the first overtone at 1976 cm^{-1} .

Assignment of the C-C stretch in $\text{CH}_2=\text{CHCF}_3$ to the band at 811 cm^{-1} was based on the spectra of similar compounds. The C-C stretch in propene is 920 cm^{-1} ,⁵ and introduction of the fluorines should lower this frequency. For example, the C-C stretch in CH_3CHO is 1113 cm^{-1} ⁶ and is lowered to 840 cm^{-1} in CF_3CHO ⁷ and 807 cm^{-1} in CF_3CFO .⁸ The only band that can be assigned as the Si-C stretch in the silicon compound was observed at 690 cm^{-1} .

The CF_3 deformations are assigned as 718 and 552 cm^{-1} , agreeing well with the values of 706 , 580 , and 531 cm^{-1} in CF_3CHO .⁷ The SiF_3 deformations can be assigned to the bands at 432 and 362 cm^{-1} , because the

only other bands near these are at 543 and 287 cm^{-1} , and these can be assigned as the C=C twist and Si-C=C bend, respectively. The Si-C=C bend in $\text{CH}_2=\text{CHSiCl}_3$ was assigned as 330 cm^{-1} .² For $\text{CH}_2=\text{CHCF}_3$, the skeletal bend is assigned as 431 cm^{-1} , whereas in $\text{CH}_2=\text{CHCCl}_3$, it was assigned as 333 cm^{-1} .¹ The only choice for the CF_3 rocking vibrations seems to be 318 cm^{-1} , whereas the corresponding bands for the silicon compound were not observed and may be below 200 cm^{-1} . The CF_3 rocks for CF_3CHO were observed at 322 and 256 cm^{-1} .⁷

Several of the observed bands of both compounds can be assigned unambiguously to the mode of vibration. The assignment of most of the other bands can be confidently made by comparison with spectra of similar compounds, and in several cases these assignments are supported by the vapor-state band contours. The lone C-H in-plane bend (Si), C-X stretch (C and Si), SiF_3 symmetric stretch, and XF_3 symmetric deformations (C and Si) are all type A bands as expected, and the C=C twist is a type C band in the silicon compound, but rather structureless in the carbon compound. The 892-cm^{-1} band in the silicon compound has a well-defined A contour, suggesting that this band is due to the symmetric SiF_3 stretch, while the 973-cm^{-1} band contour is not well defined, but may be type C.

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Spin-Lattice Relaxation in High-Resolution NMR Spectra of Carbon-13

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The measurement of nuclear spin-lattice relaxation times promises to be a useful diagnostic for the assignment of ^{13}C nuclear magnetic resonance spectra. For reasons of sensitivity and spectral simplicity, carbon-13 spectra are commonly observed under conditions where all proton-carbon splittings are removed by strong, incoherent irradiation of the entire proton resonance region¹ thus obscuring the information about the number of directly attached protons. Although this

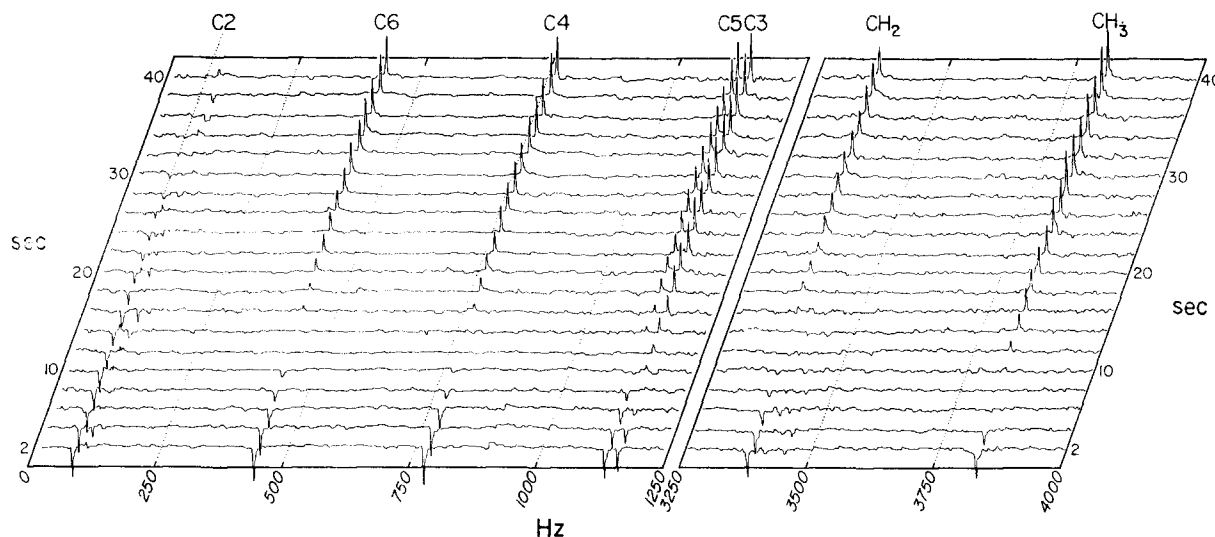


FIG. 1. A montage of carbon-13 spectra illustrating the recovery of the individual lines of 2-ethylpyridine after population inversion by a nonselective 180° pulse. The time axis represents the delay (t , seconds) between the 180° pulse and the 90° pulse used to excite the free induction signal. Each trace is the Fourier transform of four time-averaged free induction signals.

information can often be retrieved in a suitably arranged off-resonance coherent decoupling experiment,² where the multiplicity of the residual proton-carbon splittings distinguishes methyl, methylene, methine, and quaternary carbons, simplicity is sacrificed and this may become unacceptable in complicated carbon-13 spectra. In cases where dipole-dipole interaction between protons and carbon is the dominant spin-lattice relaxation mechanism, Kuhlmann *et al.*³ have predicted that carbon spin-lattice relaxation times should be simply related to the number of directly bonded hydrogen atoms.

Spin-lattice relaxation is also intimately connected with molecular motion—specifically rotational tumbling and to a lesser extent translational and internal motion. To take a practical example, preliminary measurements on a straight-chain hydrocarbon indicate a small but significant increase in carbon spin-lattice relaxation times towards the ends of the chain, presumably attributable to the shorter correlation times for the motion of these nuclei. The simplicity of carbon-13 spectra under proton noise decoupling conditions make this an attractive nucleus for this kind of study.

When the Fourier transform technique⁴ is used for carbon-13 spectroscopy, a knowledge of the general trends of the spin-lattice relaxation times is useful as a guide for setting the pulse width for optimum sensitivity. It is also important to know when significant variations of T_1 are to be expected between different lines in the same spectrum, since this can lead to apparent variations of intensity from line to line unless the experimental parameters are suitably chosen to minimize this effect⁴.

The carbon-13 spectra presented below were measured by Fourier transformation of free induction signals recorded on a Varian XL-100-12 spectrometer fitted

with a VFT-100-X accessory. Proton noise decoupling was used throughout, the sample temperature being maintained at about 49°C by a current of room-temperature air through the probe. The sample was sealed in an 8-mm tube (but not degassed) and contained about 25% by volume of acetone- d_6 for internal field/frequency regulation via the deuterium resonance. A 180° pulse inverted the spin populations, and t seconds later the recovery of the individual signals was monitored by Fourier transformation of the free induction transient after a 90° pulse, as in the scheme introduced by Vold *et al.*⁵ In practice four such transients were averaged to improve sensitivity, each 180° - t - 90° sequence being separated by a time ($T=150$ sec) long compared with the longest relaxation time to be measured. This generates a series of spectra as a function of t , and the individual recovery curves are readily visualized by stacking the spectra to give the impression of a three-dimensional diagram. A spectrum corresponding to thermal equilibrium was measured with $t=150$ sec.

Figure 1 illustrates a typical series of spectra of 2-ethylpyridine, where the aliphatic and aromatic regions were studied separately by a technique⁶ for obtaining partial spectra by the Fourier transform method. The experimental errors in the derived spin-lattice relaxation times were estimated to be less than $\pm 10\%$. Significant differences are evident between carbon sites. The carbon at position 2, having no directly bound protons, has $T_1=68$ sec, three times longer than any other carbon nuclei. As expected³ the methyl carbon is rapidly relaxed ($T_1=14.4$ sec). However the spin-lattice relaxation times of the methylene carbon and the ring carbons C4, C5, and C6 all fall into the range 21–23 sec, in spite of the difference in numbers of directly attached protons. Note the significantly

different relaxation times of C3 (15 sec) and C5 (22.5 sec). It is very difficult to assign these lines on chemical shift evidence alone and the proposed assignment is based on the assumption that the shorter T_1 results from proximity to the methyl protons, leading to a stronger dipole-dipole term.

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Nonempirical LCAO MO SCF and CI Studies of the Isomers of CH_3O^+ *

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The mass-31 ion in the mass spectra of oxygen-containing compounds has been presumed to have two distinct structures.¹⁻³ The ion corresponding to protonated formaldehyde, CH_2OH^+ , is readily obtained from primary alcohols by simple bond cleavage. Appearance potentials have established its heat of formation at around 170 kcal/mole. It has been suggested that the ion with the methoxy structure, CH_3O^+ , may be formed from methyl esters or ethers by simple bond cleavage. Appearance potentials of mass 31 from these compounds lead to a heat of formation somewhat larger than 200 kcal/mole. However, a recent study⁴ indicates that this value is too high since the mass-31 ion produced by ionization of methyl esters and ethers contains about 30-kcal/mole excess energy. Therefore,

the actual heat of formation of this ion is presently thought to be about 170 kcal/mole. Since this is about the same as the heat of formation of protonated formaldehyde, it has been proposed⁴ that the mass-31 ion from methoxy compounds also has the protonated formaldehyde structure.

Since it is possible that the agreement of the heats of formation is fortuitous and there are actually two isomers of CH_3O^+ with nearly the same energy, it seems worthwhile to investigate this possibility further by using Gaussian basis functions in the nonempirical LCAO MO SCF method of Roothaan.⁵ The basis sets we chose for the calculations are grouped Gaussian orbitals. For carbon and oxygen, the *s*-type grouped orbitals are those reported by Whitten.⁶ The *2p* orbitals are not constructed from lobe functions; instead, Cartesian Gaussian were used. These were obtained from Huzinaga's 9, 5 basis set calculations on the first row atoms.⁷ A scaling factor of 1.414 was applied to the hydrogen 1s orbitals as suggested by Fink *et al.*⁸ These basis functions are about double zeta accuracy for each of the atoms. The nonempirical LCAO MO SCF calculations were carried out using the "MOLE" Quantum Chemistry System which is a general purpose program for quantum-mechanical calculation of the electronic structure of molecules.⁹

The equilibrium geometries for the two structures were found using the 15 orbital basis set described above. Protonated formaldehyde was found to have a planar structure with bond lengths and bond angles similar to those previously predicted by Ros.¹⁰ The methoxy ion was assumed to have C_{3v} symmetry, and the bond lengths and bond angles were then varied to obtain the equilibrium configuration. These results are given in Table I.

With the geometries of the two molecules so determined, a 48-structure configuration interaction (CI) study of the protonated formaldehyde and 16-structure CI study of the methoxy ion was carried out with the same minimal basis set of 15 orbitals using the MOLE

TABLE I. Geometries and energies of CH_2OH^+ and CH_3O^+ .^a

	Bond lengths and angles			Energies	
	This work	Literature		This work	Literature
CH_2OH^+ (singlet)	CO	2.52	2.40 ^b	-113.9991	-110.53606 ^b
	OH	1.90	1.86 ^b		-113.8609 ^c
	CH	2.21		-114.0460 (CI) ^d	
	COH	120°	120° ^b	-114.0893 (S) ^d	
	HCH	126°			
CH_3O^+ (triplet)	CO	3.25		-113.9854	
	CH	2.10		-113.9972 (CI) ^d	
	HCO	102°		-114.0351 (S) ^d	

^a Bond lengths and energies are reported in atomic units.

^b Reference 10.

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^d CI stands for configuration interaction study and S stands for split-orbital calculation.