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Correlations among One-Bond Deuterium Isotope Shifts in ^{13}C NMR and C–H Stretching Frequencies in IR for Monosubstituted Methane Derivatives

Yasuki NAKASHIMA[†] and Kensuke TAKAHASHI*

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466
[†]Research and Development Department, Menicon Co., Ltd., Biwajima, Nishi-ku, Nagoya 451

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Synopsis. The effects of one bond deuterium isotope on ^{13}C NMR chemical shifts ($^1\Delta$) of the title compounds were found to be correlated with the corresponding C–H stretching frequencies(ν_{CH}) in IR spectroscopy, as follows: $^1\Delta$(ppb)= $-8.69\ \nu_{CH}$(cm^{-1})+26500.

The effects of the deuterium isotope on the ^{13}C NMR chemical shifts have been known for a long time. Recently, the true causes for these isotope shifts have been under intensive discussions.[1)] However, for polyatomic molecules, there is no suitable model for the isotope shifts, which can be used to interpret all of the observed isotope shifts. We have systematically studied the isotope shifts on ^{13}C NMR.[2,3)] As an extension of our studies, we report a correlation between $^1\Delta$ and ν_{CH}. To our knowledge, the NMR isotope shifts are related for the first time to the parameters of IR spectroscopy. Although Forsyth stated that there is no relation between $^1\Delta$ and ν_{CH} (Ref. 1b), we could find a correlation between the two parameters for a series of the title compounds.

Experimental

The isotope shifts were measured for mixtures of deuterated and undeuterated materials within an error of 3 ppb by a Varian XL-200 FT-NMR spectrometer at 50.3 MHz and about 22 °C. The IR spectra were measured for samples in the liquid phase within an error of 4 cm^{-1} using a JASCO FT/IR-8300 spectrometer. The materials were all commercially available.

Results and Discussion

The data concerning $^1\Delta$ and ν_{CH} for thirteen monosubstituted methane derivatives are given in Table 1 and are shown in Fig. 1. As can be seen in, there is a linear correlation between $^1\Delta$ and ν_{CH} with one exception. The largest deviation of CH_3NO_2 (**4**) could not yet be interpreted. The reason for this large deviation, for example, the conjugate effect or the magnetic anisotropy effect of the nitro group, can be considered.

It is well known that the C–H bond lengths can be predicted from the ν_{CH} values with high precision.[4,5)] From this knowledge, $^1\Delta$ can be related to the C–H bond lengths of the observed carbons. When a C–H bond in a molecule is shorter than others, the observed ν_{CH} will be larger than that for the latter. Thus, this relation predicts that $^1\Delta$ becomes smaller for a carbon with a shorter C–H bond. This fact strongly supports an isotope shift model proposed by Jameson and Osten.[1c)] This model assumes different anharmonic vibrational contributions for the C–H and C–D bonds. Although the energy surfaces for the deuterated and undeuterated materials should exactly coincide, small changes in the bond lengths and bond angles, which

Table 1. One-Bond Deuterium Isotope Shifts ($^1\Delta$) and C–H Stretching Frequencies (ν_{CH}) of Monosubstituted Methane Derivatives

No.	Substituent	$^1\Delta$[a)]	Ref.	ν_{CH}[b)]	Ref.
1	I	146.9	7	3029	5
2	CN	443.3	7	2979	5
3	H	579	8	2992	5
4	NO_2	684.2	7	3028	5
5	Sn(Me)$_3$	777	9	2960	5
6	SBu^n	747		2971[c,d)]	
7	COMe	751[e)]		2973[f)]	5
8	CHO	756	10	2961	4
9	C_6H_5	825.5	11	2953	5
10	OH	849.2	7	2950[f)]	5
11	CH_3	852.0	12	2950	5
12	OBu^n	903		2940[c,d)]	
13	SOMe	911[e)]		2955[d)]	

a) $^1\Delta$ were defined as follows: $^1\Delta=\delta_{CH_3}-\delta_{CD_3}$ in ppb. Thus, high field shifts give positive $^1\Delta$. b) Measured in a gas phase (see Ref. 5) in cm^{-1}. c) Estimated values from averaged C–D stretching frequencies which are multiplied by $(13/7)^{1/2}$. See Ref. 13. d) Measured in a liquid phase in cm^{-1}. e) Measured for the d_6 compounds. Then, the contribution through three bonds was assumed to be negligible. f) Averaged for two nonequivalent C–H frequencies. See Ref. 5.

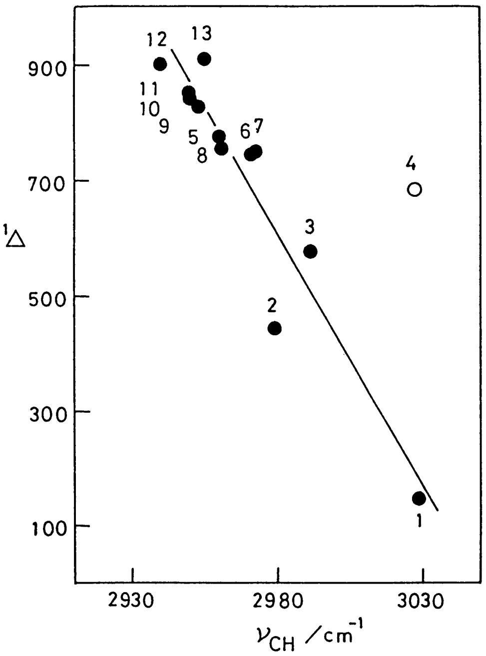

Fig. 1. Correlation of $^1\Delta$ with ν_{CH} of monosubstituted methane derivatives. With an exception of the value for CH_3NO_2, a correlated straight line is expressed as $^1\Delta$ (ppb)=26500−8.69 ν_{CH}(cm^{-1}) with r=0.945 and a standard deviation of 77 ppb.

result from averaging over a vibrational motion in an anharmonic potential well, can be expected to occur.[6] This model assumes that the potential is less anharmonic for shorter, stronger bonds. With shorter bonds, the bond shortenings upon replacement of H by D are smaller, resulting in a smaller $^1\Delta$.

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