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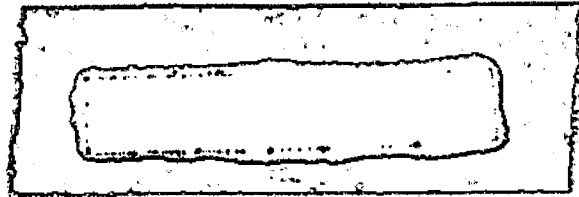
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NMR SPECTRA OF GASES

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February 1961

TEMPERATURE DEPENDENT CHEMICAL SHIFTS IN THE  
NMR SPECTRA OF GASES<sup>1</sup>

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Abstract

It is found that the chemical shifts of various gaseous compounds, using gaseous methane as a standard, vary with temperature. The slopes of chemical shift versus temperature at 50°C are tabulated for several compounds. This effect is ascribed to excitation of vibrational modes of the molecules, the protons in the excited molecules being differently shielded than the protons in the molecules in the ground vibrational states. The data are interpreted to yield approximate chemical shifts associated with the excitation of various types of modes. NMR isotopic shifts are discussed on the basis of these data.

Introduction

Recently, Gutowsky<sup>2</sup>, Tiers<sup>3,4</sup>, and Saunders<sup>5</sup> have reported several examples of an NMR chemical shift of proton and fluorine resonances resulting from an isotopic substitution in the vicinity of the nucleus under consideration. In all cases thus far reported, the resonance of the observed species moves to higher field, that is to greater magnetic shielding, when an atom in the immediate

vicinity is replaced by a heavier isotope.

It has been postulated<sup>2</sup> that this effect is the result of a change in the dynamic state of the molecule; the increased effective mass for the vibrations in which the substituted nucleus participates results in lower zero-point energies for these modes and thus in a change in the average electronic wave function. Moreover, the anharmonicity of a CH stretching mode, for example, would make the zero-point average CD distance in a molecule shorter than the zero-point average CH distance in the isotopically substituted molecule. Such a shortening of the average bond lengths might certainly bring about electronic perturbations observable several bonds away.

Gutowsky<sup>3</sup> has made a semiquantitative calculation of the chemical shift resulting from the change in the zero-point energy of the bending vibration of the CH<sub>3</sub> group. His calculation gives the proper direction for the shift and an order of magnitude agreement.

By measuring the chemical shift which accompanies the thermal excitation of vibrational modes in various molecules, we have attempted to experimentally investigate this explanation of the isotope effect.

The shifts under consideration are approximately 0.001 cps/°C in magnitude while the temperature dependent shifts due to solvent effects are usually orders of magnitude greater than this. Therefore, in order to avoid such temperature dependent solvent effects this investigation was done entirely on gaseous samples.

### Experimental

Gaseous methane was used as a reference because of the sharpness of its resonance, the large number of equivalent hydrogens per molecule, the ease of sample preparation, and because of its temperature independence. This latter point will be discussed later.

The results, tabulated in Table 1, were obtained using a Varian 60 Mcs spectrometer. The probe was equipped with a home-made variable temperature insert which readily controlled the temperature of the sample to  $\pm 2^\circ\text{C}$  over the range  $0^\circ\text{C} - 100^\circ\text{C}$ . Except for cyclobutane<sup>6</sup>, tetramethyltin<sup>7</sup>, and butadiyne<sup>7</sup> the samples were prepared from commercially available sources. For each substance a 5 mm thin-walled sample tube was made containing a mixture of the gaseous sample and gaseous methane, each if possible at a partial pressure of approximately five atmospheres. The tubes were collapsed at a distance 5 cm from the bottom so the entire gaseous sample could be thermostated in the insert. The portion of the tube above the collapsed section provided a means of spinning the sample, which was found advantageous to the resolution even with gaseous samples.

The separation between the signals had to be measured to an accuracy of a few hundredths of a cycle per second. Such accuracy can be obtained using the wobble method, but this method is not applicable to signals which are widely separated. Therefore, the following method was used which results in a precision of approximately 0.02 cps to 0.10 cps depending upon the condition of the field and

and instrument. Basically the method is the side-band technique with modifications. A Hewlett Packard audio oscillator, model 200J, was modified by placing a gang of three 5-25  $\mu\mu$  farad condensers in parallel with the three variable condensers in the tuning section. The oscillator, so modified, was stable to  $\pm 1$  part in  $10^5$ , and the frequency could be changed by increments of 1 part in  $10^5$ . By measuring the period of the signal thus generated with a Hewlett Packard frequency counter, rather than by measuring its frequency, the frequency of the signal could be rapidly obtained to better than one one-thousandth of a cycle per second.

The frequency of the signal generator was adjusted so that one sideband of the methane signal was close to, but resolvable from the signal due to the protons the shift of which was to be measured; and the amplitude of the sideband was adjusted so that the heights of the two peaks were equal. Then the sideband frequency was adjusted so that the two peaks were nearly superimposed. The resulting signal was recorded in both directions of sweep, along with the period of the audio signal. The frequency of the audio signal was changed by approximately one or two parts per  $10^5$  and the entire process was repeated. In this manner, a record was made of a pair of peaks as a function of the audio frequency. Looking at this record, it was quite easy to distinguish an envelope of these peaks. The amplitude of the signal increased from the starting point, went through a maximum, and then decreased. In this manner, the random fluctuations in the magnitude of the



signal due to changes in the homogeneity of the field, changes in the scan rate, or noise could be disregarded. The audio signal corresponding to the maximum of the envelope was selected as representing the separation between the methane and sample resonances. This method was used unless the signals were very close together, approximately 5 cps, in which case it was assumed that the scan rate was linear with time over this time interval, and the separations were measured graphically using a sideband near the peak to be measured. In all cases, five or six independent measurements were made. In a typical case, the root mean square deviation of these individual measurements was 0.06 cps and the most probable error was 0.02 cps.

The chemical shifts from methane of eleven compounds were measured as a function of temperature. Usually, five measurements were made in the temperature range 25°C to 100°C. To within the experimental accuracy, these points fell nearly on a straight line for each compound. The slopes of these lines at 50°C are tabulated in Table 1. No attempt was made to estimate the curvature of the lines, but in several cases it was apparent that the absolute value of the slope was increasing with increasing temperature.

Table 1. Temperature Dependence of Chemical Shifts  
from Methane.

Compound	$\frac{d(v_0 \delta^{\text{methane}})}{dT}$ (cps/°C)	$v_0 \delta^{\text{methane}}$ 25°C (cps)
CH <sub>4</sub>	0. ± 0.	0.
HBr	0.0000 ± 0.0005	-260.5
C <sub>2</sub> H <sub>6</sub>	0.0000 ± 0.0005	- 44.7
C <sub>3</sub> H <sub>8</sub>	-0.0080 ± 0.0027	- 3.9
C <sub>4</sub> H <sub>10</sub>	-0.0071 ± 0.0009	-113.9
C <sub>5</sub> H <sub>12</sub>	-0.0035 ± 0.0009	- 86.9
C(CH <sub>3</sub> ) <sub>4</sub>	-0.0061 ± 0.0014	- 49.2
Si(CH <sub>3</sub> ) <sub>4</sub>	-0.0125 ± 0.0015	- 8.4
Sn(CH <sub>3</sub> ) <sub>4</sub>	-0.0102 ± 0.0025	- 5.9
C <sub>6</sub> H <sub>6</sub>	-0.0087 ± 0.0014	- 80.1
CH <sub>3</sub> CCCH <sub>3</sub>	-0.0047 ± 0.0008	- 87.7
C <sub>2</sub> H <sub>4</sub>	+0.0038 ± 0.0015	-310.6

### Discussion

The chemical shift of HBr is 228 cps from HCl and 260 cps from CH<sub>4</sub> at 60 Mc<sup>8</sup>. It has been suggested by Pople et. al.<sup>8</sup> that this large chemical shift must be due to a large extent to the operation of the neighbor-anisotropy effect. On this basis it seems very unlikely that the chemical shift of the upper vibrational state from the ground state in HBr should be more than 100 cps. Let  $\Delta$  be defined as the chemical shift of the upper vibrational state from the ground vibrational state. Assuming  $|\Delta(\text{HBr})| < 100$  cps and remembering that the vibrational frequency of HBr is  $2390 \text{ cm}^{-1}$ , one readily calculates that  $|dv/dT|$  for HBr is less than  $0.0001 \text{ cps}/^\circ\text{C}$  where  $\nu$  is the resonance frequency at 14,092 gauss. Throughout this discussion we assume in addition that in the gaseous phase there are only free, unassociated molecules, and therefore, no other effect causes a  $dv/dT$  of comparable magnitude.

The line width of the signal from HBr is several cps. For this reason measurements made using it as a standard are somewhat difficult. Therefore, methane was adopted as a secondary standard. It is apparent from Table 1 that methane is temperature independent with respect to HBr, and is therefore temperature independent on an absolute basis to within our experimental accuracy.

The NMR resonance of most of the compounds under consideration are indeed temperature dependent. In general, the resonance shifts to low field as the temperature is increased.

Let  $\Delta_1$  be the shift associated with exciting the  $i^{\text{th}}$  vibrational mode of a molecule,  $\delta^{\circ}$  the shift from methane of the ground vibrational state,  $\nu_1$  the vibrational frequency associated with the  $i^{\text{th}}$  vibrational mode,  $\nu_0$  the spectrometer frequency, and  $g_1$  the degeneracy of the  $i^{\text{th}}$  mode. We can then write:

$$\nu_0 \delta = \frac{\nu_0 \delta^{\circ} + \sum_1 g_1 e^{-(h\nu_1/kT)} (\Delta_1 + \nu_0 \delta^{\circ})}{1 + \sum_1 g_1 e^{-(h\nu_1/kT)}} \quad (1)$$

where  $\delta$  is the chemical shift from methane. When all of the vibrations with sizeable  $\Delta$ 's have  $\nu$ 's greater than  $200 \text{ cm}^{-1}$ , and when we are in the temperature range around  $50^{\circ}\text{C}$ , this can be simplified to:

$$\nu_0 \delta = \nu_0 \delta^{\circ} + \sum_1 g_1 \Delta_1 e^{-(h\nu_1/kT)} \quad (2)$$

and

$$\frac{d\nu_0 \delta}{dT} = \sum_1 g_1 \Delta_1 \left( \frac{h\nu_1}{kT^2} \right) e^{-(h\nu_1/kT)} \quad (3)$$

That is, there is an additive contribution to  $d\nu_0 \delta / dT$  from each of the various modes of vibration.

The question of degeneracy is somewhat complicated by the following consideration. Consider a single hydrogen atom vibrating against a carbon skeleton. There is a  $\Delta$  associated with exciting this mode of vibration. Now consider two identical hydrogen atoms attached to the same carbon atom. In order to achieve the same observed chemical shift of the two hydrogen nuclei, one would have to excite both the symmetric and antisymmetric stretching modes. The  $\Delta$  associated with either of these two modes would be

approximately one half of the  $\Delta$  associated with the stretching mode of a single hydrogen atom. Therefore, if one hopes to assign a given  $\Delta$  to a given kind of vibrational mode, one must collect terms in the sum of equation (3) which deal with a given kind of vibration, eg  $\text{CH}_3$  parallel deformations or  $\text{CH}_2$  deformations, and consider this set of terms as a single contribution. One should then use an average of the individual vibrational frequencies, assign a degeneracy of one, and assign a  $\Delta_{\text{eff}}$  to this average mode. In the case of a single group,  $\Delta_{\text{eff}}$  is equal to the chemical shift brought about by exciting all of the modes of one kind in that group. These  $\Delta_{\text{eff}}$ 's should not depend upon the symmetry of the molecule, but only upon the type of motion involved.

Over the temperature range studied it is impossible to gain much information about  $\Delta_{\text{eff}}$  for any mode the frequency of which is above  $2000 \text{ cm}^{-1}$  since these modes are always so lightly populated that the term in the sum for  $\text{dv. } \nu/dT$  associated with them is less than our experimental error if  $|\Delta_{\text{eff}}| < 130 \text{ cps}$ . This seems reasonable in that all organic compounds have resonant frequencies in a range of approximately 600 cps at 60 Mcs. Therefore, although exciting such modes as the CH stretching mode is probably very effective in causing a chemical shift, the effect is too small to be measurable in the temperature range under consideration.

Methane: The bending modes in methane are at  $1526 \text{ cm}^{-1}$

and  $1306 \text{ cm}^{-1}$ . The temperature dependence of the chemical shift of methane is  $0.0000 \pm 0.0005 \text{ cps}/^\circ\text{C}$ . Since both of these modes only involve changing H-C-H bond angles, one would expect  $\Delta_{\text{eff}}$  for these two modes to be of the same sign. This limits the  $\Delta_{\text{eff}}$  for each of the bending modes in methane to less than 10 cps in absolute value.

Ethane: Again, the temperature dependence of the chemical shift in ethane is  $0.0000 \pm 0.0005 \text{ cps}/^\circ\text{C}$ . This may come about as an accidental, exact cancellation of two or more temperature dependent terms of opposite sign, but this seems highly unlikely; particularly since a consistent picture can be presented by assuming all  $\Delta_{\text{eff}}$  are negative except for modes involving delocalization of multiple bonds. It is therefore assumed that for ethane the individual terms in the sum of equation (3) do not cancel each other, but in fact are individually zero to within our experimental error. One then is led to the following limits on the absolute value of  $\Delta_{\text{eff}}$  for the various vibrations in ethane:  $|\Delta_{\text{eff}}|$  for  $\text{CH}_3$  perpendicular deformation is less than 17 cps; for the  $\text{CH}_3$  parallel deformation, it is less than 13 cps; for the  $\text{CH}_3$  wag, it is less than 3 cps; and for the C-C stretch, it is less than 3 cps.

In Gutowsky's semiquantitative calculation<sup>2</sup> of the contribution of the H-C-H bends, a  $\Delta_{\text{eff}}$  is predicted for these modes of approximately 1 cps. Using this calculated order of magnitude, it must now be assumed, only, that the

contribution to the chemical shift due to the  $\text{CH}_2$  wagging modes does not exactly cancel out the contribution from the C-C stretching mode. One would expect these two modes to result in quite different orders of magnitude. Therefore, this assumption seems very reasonable.

**Cyclic compounds:** In this series of compounds the temperature dependence of the chemical shift becomes smaller as the size of the ring is increased. This immediately implies that the low lying ring deformation modes have very small  $\Delta_{\text{eff}}$ 's since the larger the ring, the lower the ring mode frequencies become. By comparison with the bending modes in methane and ethane, and with the predictions of Gutowsky's calculation<sup>a</sup>, it seems unreasonable that the absolute value of  $\Delta_{\text{eff}}$  for the  $\text{CH}_2$  deformations should be greater than 10 cps. This would result in a negligible contribution to  $dv_{\text{c}}\delta/dT$ . In comparison with ethane again,  $|\Delta_{\text{eff}}|$  for the C-C stretching modes is probably less than 3 cps which also gives a negligible contribution to  $dv_{\text{c}}\delta/dT$ . One must therefore look to the  $\text{CH}_2$  bending modes for the cause of the temperature dependent chemical shift. In Table 2 are tabulated the averages of these modes for the three compounds.

Table 2. Average Infrared Vibrational Frequencies for  
CH<sub>2</sub> Bending Modes in Cyclic Hydrocarbons.

Mode	Cyclopropane	Cyclobutane	Cyclopentane
CH <sub>2</sub> rock	1000 cm <sup>-1</sup>	1050 cm <sup>-1</sup>	1055 cm <sup>-1</sup>
CH <sub>2</sub> wag	1050	1250	1250
CH <sub>2</sub> twist	870	1080	1100



It can be seen that the  $\text{CH}_2$  bending modes are the lowest in frequency in the cyclopropane and are the highest in cyclopentane. Thus if these modes all had the same magnitude of  $\Delta_{\text{eff}}$  associated with them, this would result in the proper trend of temperature dependence of chemical shifts with ring size. If one assumes that the  $\Delta_{\text{eff}}$ 's for the three modes in a given compound are equal one calculates  $\Delta_{\text{eff}} = -14, -16, -9$  cps for cyclopropane, cyclobutane, and cyclopentane respectively. While the experimental agreement is not good, it at least makes one believe that these are the modes which are mainly responsible for the temperature dependence, and that  $\Delta_{\text{eff}} = -13$  cps is of the proper order of magnitude for these modes. Indeed, it is not surprising that  $\Delta_{\text{eff}}$  varies a good deal within this series due to the change in electronic configuration in the CH bonds due to ring strain.

Tetrahedral compounds: Again by comparison with ethane one would expect the  $\text{CH}_3$  perpendicular and parallel deformations, the  $\text{CH}_3$  wags, and the skeletal stretching modes to contribute a negligible amount to  $dv_{\text{C}}/dT$ . The torsional modes are so low in frequency that they must involve very small changes in the electronic structure. Therefore, their contribution to  $dv_{\text{C}}/dT$  is expected to be very small. This is in agreement with the observation for the low lying ring modes in the cyclic compounds.

The temperature dependent shift must therefore come about as a result of the skeletal bending modes. Making this assignment, one calculates for the skeletal bending modes

$\Delta_{\text{eff}} = -0.6, -1.1, -1.1$  cps for tetramethylmethane, tetramethylsilane, and tetramethyltin respectively.

The near equality of these three values is reassuring considering the differences between the three molecules.

Multiple bonded compounds: In acetylene both the CH stretch and the  $\text{C}\equiv\text{C}$  stretch are so high in frequency that even if  $\Delta_{\text{eff}} = \pm 100$  cps for these modes, the observed temperature dependence would be negligible. The only modes left are the CH bending modes and these must account for  $-0.0083$  cps/ $^{\circ}\text{C}$ . This implies that  $\Delta_{\text{eff}}$  for these bending modes is  $-17$  cps which is quite high compared to the bending modes in the  $\text{CH}_3$  group, and is even quite high compared to the bending modes in the  $\text{CH}_2$  group. This is probably due to the proximity of the  $\pi$  electrons in the triple bond. These electrons will be responsible for the proton's being less shielded when it is off the figure axis of the molecule than when it is on<sup>8</sup>. Therefore, exciting the CH bending modes will cause the protons to spend a greater fraction of their time off the figure axis, thus moving their resonance downfield, in excess of the shifts observed in the other CH bending modes cited above.

In dimethylacetylene, again assuming that the  $\text{CH}_3$  deformation modes, the  $\text{CH}_3$  rocking modes, and the C-C stretching modes contribute only a very small amount as in ethane, one must assign  $\Delta_{\text{eff}}(\text{skeletal modes}) = 4.2$  cps. This seems a rather large effect compared to other shifts calculated for skeletal modes such as the C-C stretch.

However, when one considers that again bending the molecule interferes with the  $\pi$  electrons, one can believe that 4.2 cps is not too large a  $\Delta_{\text{eff}}$  for the skeletal bends.

In ethylene, a positive shift is observed with increasing temperature. One can make a good estimate of the  $\Delta_{\text{eff}}$ 's for the  $\text{CH}_2$  modes from the cyclic compounds. Again, the frequency of the CH stretches and the C=C stretch are too high to show up as a temperature variation of the chemical shift. The  $\text{CH}_2$  rocks and wags should have  $\Delta_{\text{eff}}$ 's of about 20 cps taking into account the  $\pi$  electrons. All of these contributions combine to give a  $dv_{\text{obs}}/dT$  of approximately  $-0.0070$  cps/ $^{\circ}\text{C}$ . The experimentally observed  $dv_{\text{obs}}/dT$  of  $+0.0038$  cps/ $^{\circ}\text{C}$  varies from this by  $0.0108$  cps/ $^{\circ}\text{C}$ . This large upfield shift must result from the twisting mode about the double bond. As this mode is activated, the double bond character of the bond should be decreased and the electron density in the vicinity of the protons should be increased causing an upfield shift as observed. This interpretation is of course making the naive assumption that greater electron density provides greater shielding which is not precisely true. On the basis of the above calculations  $\Delta_{\text{eff}}$  for this twisting mode in ethylene is  $+ 36$  cps.

#### Conclusions

Exciting a vibrational mode in a molecule does in

general cause a chemical shift of protons which are in the vicinity of the excited mode.  $\text{CH}_3$  and  $\text{CH}_2$  deformation modes seem to have small  $\Delta_{\text{eff}}$ 's while  $\text{CH}_2$  rocks, wags, and twists have  $\Delta_{\text{eff}}$ 's of approximately -13 cps.  $\Delta_{\text{eff}}$  for skeletal bending modes in compounds like tetramethylmethane are approximately -1 cps.  $\Delta_{\text{eff}}$  for CH bends in a compound with the structure  $=\text{C}-\text{H}$  is increased to about -17 cps, primarily due to the anisotropic susceptibility of the  $\pi$  bond. In structures where the proton under consideration is directly attached to a double-bonded carbon atom, when modes which decrease the double bond character are excited, this results in an increased shielding at the proton. In the case of ethylene,  $\Delta_{\text{eff}}$  for the twisting mode seems to be about +36 cps.

It is evident that since exciting vibrational modes can bring about chemical shifts of from 0 to 40 cps, isotopic substitution can bring about sufficient change in zero-point vibrations to cause a chemical shift of the observed magnitude. It is to be noted that changing the dynamic state of modes other than hydrogen bending modes can result in substantial chemical shifts of the protons, and therefore one can not hope to explain isotopic shifts by considering the changes brought about in only the bending modes.

Footnotes

1. This research was supported in part by the United States Atomic Energy Commission.
2. H. S. Gutowsky, *J. Chem. Phys.*, 31, 1683 (1959).
3. G. V. D. Tiers, *J. Am. Chem. Soc.*, 79, 5585 (1957).
4. G. V. D. Tiers, *J. Chem. Phys.*, 29, 963 (1958).
5. M. Saunders, J. Plostnieks, P. S. Wharton, and H. H. Wasserman, *J. Chem. Phys.*, 32, 317 (1960).
6. The sample of cyclobutane was kindly provided by Professor W. Gwinn of this department.
7. The samples of tetramethyltin and butadiyne were kindly provided by California Research Corporation, Richmond, California
8. W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, 28, 601 (1958).
9. See the discussion of the effect of  $\pi$  electrons on protons in the vicinity: J. A. Pople, W. G. Schneider, and H. J. Bernstein; "High Resolution Nuclear Magnetic Resonance," pp. 176-179, McGraw-Hill Book Company, Inc., New York, 1959.

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