

RECENT RESULTS OF CHEMICAL INTEREST FROM MICROWAVE SPECTROSCOPY

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In this paper I should like to talk about some recent applications of microwave spectroscopy to the chemistry of some small molecules, mostly inorganic compounds. But first I wish to give a brief summary of some of the characteristics of microwave spectroscopy which are particularly important in chemical research.

Thus, one major advantage is the highly characteristic nature of the spectra which are obtained. It is normal to measure observed frequencies to a tenth of a megacycle or better. The region of the spectrum which is not too difficult to cover runs from perhaps 5 to 10 kilo megacycles at the lower limit to anywhere from 50 to 100 kilo megacycles and on up. If we confine ourselves to the region which we happen to be able to cover most conveniently in our own laboratory at Harvard, there is a range of at least 50,000 megacycles. With an accuracy of a tenth of a megacycle, this means that there are something like a half million different frequencies which might be distinguished. This can be compared with the situation in the infrared where with good instruments one might measure frequencies to about a wavenumber in typical cases and have a frequency range available of perhaps 3,000 wavenumbers, so that there are 3,000 possible measurements instead of 500,000.

In order to make this comparison and argument complete, we need to say something about the richness of microwave spectra. This varies greatly from one molecule to another. Water, for example, has only one observed line in the easily reachable region, whereas large complicated molecules can have almost continuous spectra. These latter, however, naturally tend to be extremely weak. I think it is conservative to consider a substance having on the average one reasonably strong transition every 50 megacycles. This is quite a rich spectrum and most of the simple molecules will have many fewer lines. Suppose that we measure a certain number of transitions, let us say n , and suppose that we measure these to an accuracy of a tenth of a megacycle. What are the chances that we could confuse the identification of two molecules? *Table 1* shows the calculations—admittedly very primitive with rather arbitrary assumptions. Nevertheless, it is clear that an enormous number of molecules can be sharply and definitely distinguished by measuring, to normal accuracy only a quite small number of transitions. This, of course, applies only if we know that we are dealing with a pure substance and not a mixture. However, simple mixtures would not greatly disturb this calculation.

Table 1. Probability of mis-identification of a compound

| | |
|--|-----------------|
| Prob. A at $\nu_1 \pm \epsilon \nu$: | P_1 |
| Prob. A at $\nu_1, \nu_2, \dots, \nu_n$: | P_1^n |
| Prob. not above: | $1 - P_1^n$ |
| Prob. not above (N cpds): | $[1 - P_1^n]^N$ |
| Prob. at least one cpd at ν_1, \dots, ν_n : | |
| $1 - [1 - P_1^n]^N \cong NP_1^n$ | |
| $= 5 \times 10^{-6}$ if $N = 20,000, n = 4, P_1 = 0.004$ | |

A general atlas¹ of observed frequencies is urgently needed. I understand that work is underway on such an atlas at the National Bureau of Standards in Boulder, Colorado, but it would be very desirable if this project could be speeded up.

The next point is that the lines are quite sharp so that in a general sort of way there is relatively little overlapping. Suppose that we ask how many different components in a mixture can we hope to identify? Using the assumptions that each component has on the average one line per fifty megacycles and that the lines are a megacycle wide, we find that we might have to look for 20 to 30 known transitions for a given species in order to be reasonably sure to find one of them not overlapped by a line of some other substance in a mixture of 100 components (see Table 2). Naturally, if we start mixing too many things together, we can't have very much of each present and the spectra of some of the species would become quite weak.

Table 2. Probability of overlapping n lines by N compounds

| | |
|--|-----------------|
| Prob. A at $\nu_1 \pm \epsilon \nu$: | P |
| Prob. not A : | $1 - P$ |
| Prob. none of N at ν_1 : | $(1 - P)^N$ |
| Prob. at least one: | $1 - (1 - P)^N$ |
| Prob. none at $\nu_1, \nu_2, \dots, \nu_n$: | |
| $1 - [1 - (1 - P)^N]^n \cong 0.01$ | |
| if $P = 0.02, N = 50, n = 10$ | |

That raises another question: how small a percentage of a given substance can we hope to recognize in a sample? This will depend very much indeed on the intrinsic intensity of the spectral lines. A great many of the molecules which have been observed and studied have some transitions with absorption coefficients of the order of 10^{-7} per centimetre. This is reasonably typical. There are, of course, much stronger lines of selected substances, some even a thousand times stronger, but these are special substances and I am trying to be more general. Spectrometers² have been built with a claimed sensitivity of 10^{-10} per centimetre. Therefore, a substance with a coefficient of 10^{-7} would be detectable at about a tenth of a percent concentration under these circumstances. By going to higher frequencies, one should be able to improve this by at least a factor of ten, and perhaps a factor of a hundred. By developments in spectrometers which one can hope for, a gain of another factor of ten is reasonable. Combining these, I believe one can expect to see parts per million of many substances in the not too distant future.

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Another characteristic that can be important is the total quantity of sample required. Quite commonly, microwave spectrometers use an absorption cell with a cross-section of perhaps three square centimetres and a length of perhaps 300 centimetres. The volume is therefore about a litre at a pressure of 10 microns, which is not excessively low. This is approximately a micromole, but, if we are able to detect a component present in 1 percent concentration, then we are dealing with a 100th of a micromole which would therefore usually be a fraction of a microgramme. Examples³ are reported in which a much smaller quantity than that was present in the vapour volume of the absorption cell. One must naturally add to this the material which is necessarily adsorbed on the surface of the waveguide and the amounts in the manifold of the system (which could be reduced very much by specially designed equipment). It seems, therefore, certain that one can study the microwave spectrum of a small fraction of a microgramme. The limitation is most likely set by the handling of the sample rather than the sensitivity of the apparatus itself.

One final characteristic will be mentioned and that is the ability to handle substances with very short lifetimes. The shortest lifetime so far studied is probably the OH radical originally observed by Townes' group in the laboratory at Columbia⁴. This was done by producing the OH radicals in an electric discharge and flowing them through the waveguide. Calculations showed that the residence time in the waveguide was something of the order of a tenth of a second. More recently it has been claimed that the OH is produced in the waveguide itself by the reaction of hydrogen atoms and that the lifetime of OH is really much shorter. In any event, there have been numerous cases of molecules with lifetimes of a minute or less being conveniently studied by a flow system. Examples are listed in *Table 3*.

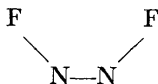
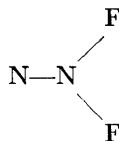
Table 3. Some short-lived species studied by microwaves

| | <i>Reference</i> |
|-------------------------------|------------------|
| OH | 4 |
| CS | 5 |
| O ₃ | 6 |
| O ₂ F ₂ | 7 |

I should not end this list without recalling the well-known limitations of pure rotational microwave spectroscopy. It is restricted to polar substances with at least 0.01 mm vapour pressure at reasonable temperatures. The molecule must not be very large and a few diatomic hydrides are excluded because they are too small.

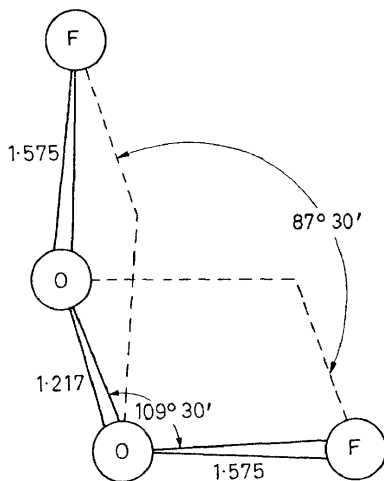
I should now like to discuss briefly a number of specific investigations which have recently been carried out.

A study of the less stable isomer of N₂F₂ is presently in progress in our laboratory at Harvard by Kuczkowski. He has so far obtained quite strong evidence that this compound is in the *cis* form, shown in *Figure 1*, instead of the *trans* form (*Figure 2*) which has been claimed by some. The evidence for this comes from alternating intensities and also from the existence of a low vibrational frequency not taken into consideration in the previous infrared analysis. Incidentally, there was a small technical extension of the art

Figure 1. Proposed *cis* structure for N_2F_2 Figure 2. Proposed 1-1 structure for N_2F_2

here because it was necessary to determine relative intensities of rotational transitions which could not be completely modulated by the Stark voltages available to us.

Jackson completed work on the molecule O_2F_2 which has the structure shown in Figure 3. This is a very interesting molecule from several points of

Figure 3. Structure of O_2F_2

view. It is quite unstable so that it presented some technical difficulties. It has the more-or-less expected hydrogen peroxide-like structure. What is unusual about it is the quantitative nature of the bond lengths. The oxygen—oxygen distance is exceptionally short, practically the same as in the oxygen molecule, while the O—F distance is unusually long. Knowing the structure, it is possible to give some qualitative interpretation of it, but I believe that the detailed structural parameters would not have been predicted in advance. Nevertheless, the study of the literature suggests that somewhat similar effects are taking place in other related molecules.

While studying some sulphur—fluorine—nitrogen compounds, Kirchhoff found some microwave lines which seem to be associated with a mass spectral peak which he could not at first account for. He ultimately was able to identify these with the known compound⁸ HNSO which is now reported to be a hydrolysis product of SNF^9 . The structure Kirchhoff obtained for HNSO is shown in Figure 4. Note that he finds the *cis* form although it is not impossible that some of the *trans* form exists as well. Furthermore, another species with the hydrogen bonded to the oxygen is claimed in the literature¹⁰.

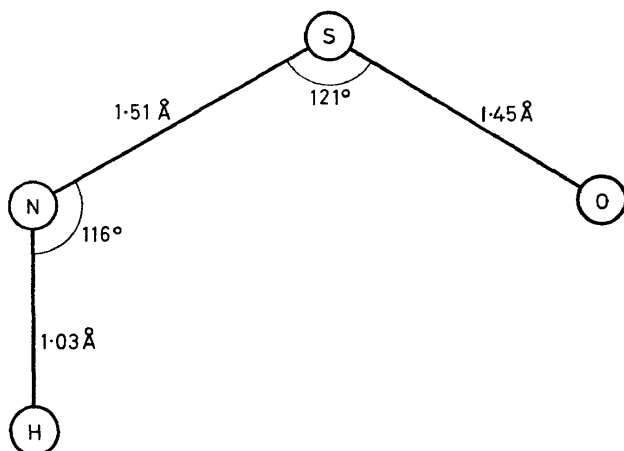
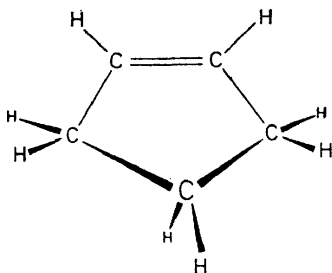


Figure 4. Approximate structure of HNSO

While studying O_2F_2 , Jackson found that certain new microwave lines grew in after a few minutes' time. These corresponded to a quite stable substance which at first he could not identify. By using these lines as an indicator of concentration and making some simple distillations a fairly clean mass spectrum was obtained. From this he inferred that the compound might be OCF_2 which he then confirmed using a brief published report or the moments of inertia of this molecule¹¹. The question arose as to where the carbon had come from. Later experiments demonstrated that O_2F_2 reacts with the Teflon insulation in our waveguide even at dry ice temperatures. The amusing thing is that this reaction turned out to be the easiest way to make the ^{18}O species and study its microwave spectrum so that the complete study of this molecule has now been made in collaboration with Laurie at Stanford University.

Rathjens' work on cyclopentene was published recently¹². This was a very difficult microwave investigation because of the weakness and richness of the spectrum of this molecule. Nevertheless, Rathjens finally succeeded in deciphering it and came up with the result that cyclopentene, shown in Figure 5, is slightly non-planar as might perhaps be expected. This molecule

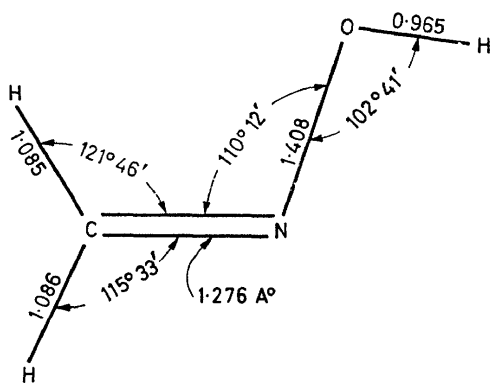


Cyclopentene

Figure 5. Structure of cyclopentene (non-planar ring)

adds to the several others including trimethylene oxide¹³, formamide¹⁴, cyanamide¹⁵, and others for which there have been demonstrated small deviations from planarity by the use of rather delicate interpretations of microwave spectra.

A deviation from simple geometry of another type is displayed by formaldoxime, which has recently been completed by Levine at Harvard. *Figure 6* shows the dimensions which he obtained from an exhaustive set of isotopic



Tilt in formaldoxime

Figure 6. Structure of formaldoxime showing tilt

species. The critically interesting point is the tilt in the methylene group which these numbers show. We have tried to see whether zero-point effects could possibly account for this apparent tilt but this does not seem to be possible. We therefore believe that it is a real tilt, possibly caused by steric repulsion between the oxygen and one of the hydrogens of the methylene group, but it may well involve attraction by the unshared pair on the nitrogen, as is claimed in several cases of CH_3 tilt¹⁶.

Recently, we have developed a method for determining relative intensities to a quite good level of accuracy with a Stark effect spectrometer. Esbitt and Cox applied this to some observed vibrational satellite lines in ketene, and the results are quite surprising. These show that the infrared spectroscopists completely missed one of the low-frequency fundamentals and, consequently, wrongly assigned some of the others. From the microwave results on all the deuterated and undeuterated species, a set of three low vibrational frequencies are predicted. Wilson at Tufts University kindly allowed the use of his low-frequency, low-temperature infrared spectrometer on these compounds and the result was a complete confirmation of the microwave frequencies (see *Figure 7*). There are probably many other molecules to which this technique could be applied. It is, therefore, one of the ways in which pure rotational spectra can determine vibrational frequencies, sometimes more reliably than by their direct study in the infrared.

Another way in which vibrational information can be obtained from microwave spectroscopy is through the study of centrifugal distortion. For small

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light molecules and particularly for triatomic molecules, such as F_2O , H_2O , H_2S , H_2Se , Cl_2O , ClO_2 , SO_2 , NO_2 , O_3 , centrifugal distortion effects can be very large and accurately measurable. The basic theory has existed for a long time but recently Pierce at Notre Dame has developed computer programmes which make it really practical to apply the existing theoretical formulae to such data. The results are very gratifying. F_2O has been worked out very thoroughly using data which Jackson sent to Pierce. The force

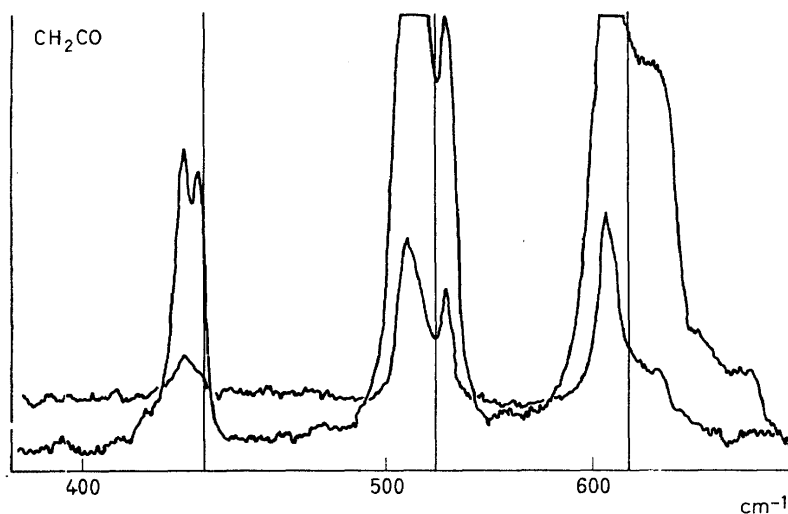


Figure 7. Low temperature infrared spectrum of ketene; vertical lines at frequencies calculated from microwave intensities

constants obtained from the centrifugal distortion data give calculated vibrational frequencies which are surprisingly good. It may be possible in the future to get anharmonic force constants out of this information using the sixth power terms.

I should like to mention one other type of information which we have been obtaining from the analysis of microwave spectra. This concerns rotational isomers. These isomers, on which so much pioneer work has been done in Japan¹⁷, show up very clearly in microwave spectroscopy. Although they rapidly transform from one form to another, the lifetime is normally longer than the time between collisions, which is all that is required in order that they show completely distinct microwave spectra just as if they were completely stable separate species. Consequently, a greater deal of information can be obtained about the separate rotational isomers including their structure, dipole moments, methyl group barriers, low vibrational frequencies, *etc.* I will not go further into this point because Hirota is describing his own results at a later session.

A problem which we have under investigation at this moment is a microwave study of the existence, structure, dipole moment, bonding pattern and chemistry of a claimed compound which is probably either NSF or SNF. Kirchhoff has prepared an impure specimen, observed and assigned quantum

numbers to many lines, and hence has the moments of inertia. These are most reasonably explained by a bent form NSF. The sulphur isotope data should be conclusive. Incidentally, the microwave data is not in agreement with an electron diffraction report.

These examples are not unique in any special way and many others are available from laboratories all over the world which show the power of microwave spectroscopy for characterizing, identifying, and determining the structure, dipole moment, lower vibrational frequencies, and many other properties of simple molecules. This is true even for molecules of very short lifetime which cannot be obtained pure and often only in very small quantities.

I should like to end my paper by speculating a little concerning the future. I hope the future I speak of is the very near future but I am not quite sure of this. At the present time, we have gained a good deal of experience in assigning quantum numbers to a few observed transitions in fairly simple molecules whose identity we know and whose structure we usually know approximately. In addition, it is customary to have reasonably pure samples. Some illustrations can be quoted of studies of known substances of approximately known structure which were present in not very pure form. Furthermore, there have been molecules studied in pure form whose chemical identity was known in advance but whose structure turned out to be somewhat surprising. What no one has yet done, to my knowledge, is to analyse the spectrum and assign quantum numbers and determine the structure of an unknown chemical substance. I believe that this can eventually be done with a little luck. It is not simple and it is certainly true that, in analysing microwave spectra today, everyone makes considerable use of the information available in advance concerning the compound being studied. Theoretically, it is conceivable that careful study of the Stark effect of many transitions would lead to an assignment of these transitions and the determination of the moments of inertia of the species. Furthermore, lines due to various isotopic species occurring in natural abundance might next be identified. Accurate relative intensity measurements might identify which elements were responsible for the isotopic species. Moreover, the moments of inertia of these isotopic species, compared with the original moments, will give the Cartesian coordinates of the atom in question. If all the atoms in the molecule had naturally occurring isotopic forms, this procedure would determine the complete structure and chemical identity of a molecule about which we had no information except its complete microwave spectrum. I appreciate that this is rather an idealized case. Nevertheless, there are other pieces of information which can be obtained directly from the spectrum alone. If there are quadrupolar nuclei such as chlorine, bromine, iodine, or nitrogen, these will usually signal their presence by a hyperfine structure. Alternating intensities can be used to show that there are two or more equivalent sets of atoms. Preparations can be made using various isotopic reagents. Chemical reactions can be carried out with sub-microgramme quantities of an unknown substance, even in a mixture, and the resulting products may be identifiable by microwave spectroscopy. Certainly the fact that a reaction has occurred is immediately evident from the disappearance of the characteristic lines of the unknown substance. Some

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physical properties such as the vapour pressure can be determined approximately by observing the microwave spectrum and it is even, in principle, possible to estimate the molecular weight.

The dipole moment and lower vibrational frequencies can be obtained. What I am suggesting here is that a whole series of techniques more-or-less analogous to those which the radio chemists long ago developed for studying the properties of trace quantities of materials, may likewise be developed using microwave spectroscopy as a tool. We have not reached this state of affairs yet but I see no reason why further development of spectrometers making them simpler and easier to use and perhaps more sensitive, further development of theory so that it becomes easier to assign quantum numbers to observed transitions, and further general experience may not all combine to bring about the realization of these possibilities. But whether my prophecies for the future are correct or not, I maintain that microwave spectroscopy is one of the most powerful tools we now have for the study of small chemical substances, known or unknown.

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