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UNCLASSIFIED
MOLECULAR BEAM RADIOFREQUENCY SPECTRA
OF MOLECULES
Report for Period
June 1, 1954 to August 31, 1954
Contract No. 6N-onr-248
Task Order 11
September 1954
1. Summary

Measurements were made of the variation with vibrational state of the spin-rotation constant of F in Li\(^{6}\)F. A new two-chamber oven was constructed to reduce polymerization. Tests are being conducted to see if the mass spectrometer in the apparatus can be used for leak hunting. The possibility of using an electric resonance apparatus as a high precision voltmeter or voltage standard is discussed.

2. Vibrational Effects in Li\(^{6}\)F

In June Mr. Kastner and Mr. Russell recorded the spectra of Li\(^{6}\)F arising from the 2,0 \(\rightarrow\) 2,2 transitions in the vibrational states \(v = 0,1,2\). The spectrum for each vibrational state consists of two lines separated by a frequency equal to the spin-rotation constant of F. An analysis of the spectra revealed a change of less than 1 percent in this constant between \(v = 0\) and \(v = 1\), and a decrease in its value from \(v = 1\) to \(v = 2\) of 6 percent. This kind of change has not been observed in either the molecular or nuclear-molecular constants of any other molecule; these latter constants usually change in a nearly linear fashion. This odd behavior in the spin-rotation constant of LiF has led to an interest in its value for \(v = 3\). At the time the data was taken the spectrum for \(v = 3\) was too faint to observe. However, there is some hope that with improved conditions this spectrum may be obtained and we are presently attempting to get it.

3. Polymerization of Lithium Bromide

In our last report mention was made of the possibility that our difficulties in observing the spectra of LiBr arose from polymerization of the molecules. Since then we have learned from Mr. Miller at Columbia University that a rather high degree of polymerization (mostly dimerization) does occur in LiBr and presumably in all of the lithium halides. He found, under his
conditions of operation (he used a two chamber oven), that about 76% of his 
LiBr beam consisted of diners. If we assume that polymerization is the only 
effect reducing the intensity of our spectra, then we would conclude that 
under our conditions about 99% of the beam was polymerized.

A means for reducing the polymerization of molecular beams has been 
developed by Kusch and Côté who built a two chamber oven for this purpose. 
In their oven the slits were heated to a different temperature from the solid 
(or liquid) charge. Thus the temperature and pressure of the beam were inde- 
dependent variables. We have constructed such an oven and expect to test it in 
the near future.

4. Vacuum Problems

During most of July and August we have been beset with vacuum problems. 
One of our new liquid air traps developed a leak in the bottom and had to be 
resoldered. In the course of uncovering this difficulty we decided to put new 
oil in the diffusion pumps. The old oil was very dark and had been in the 
apparatus ever since it was put into operation five years ago. The only 
 improvement noted as a result of this change has been a lower pressure on 
the fore-vacuum side of the pumps. As there are still some undiscovered 
leaks it is too early to say whether the pump oil change has resulted in any 
improvement in the vacuum on the high vacuum side of the pumps.

5. Mass Spectrometer as a Leak Detector

The use of a mass spectrometer for leak detection is by now an ancient 
technique. However, we have never tried to use for this purpose the mass 
spectrometer which is a part of our apparatus. The reason for our timidity 
has been that the ion gun seems to be very unsuitable for this purpose and we 
have eventually found our leaks with the aid of the ionization gauge. Our 
present prolonged period of unsuccessful leak hunting, however, has driven 
us to try the use of our mass spectrometer for leak hunting.
The preliminary tests conducted by Mr. Russell are very encouraging. Helium was admitted to the system by means of the controlled leak described in an earlier report. Two mass peaks which were sensitive to the He pressure were discovered with the mass spectrometer. Why there are two peaks is not understood, but they may be a consequence of the unsuitable ion gun geometry; i.e., unsuitable for use in a combined ionizer and accelerator of ions.

6. Atomic Beams Conference

All of us attended the conference on atomic beams held August 18, 19 at Brookhaven National Laboratory. Nearly everyone in the country working on molecular and atomic beams was present at the conference and a number of very interesting papers were presented. I feel that the conference was invaluable to our group in its educational effects and in the amount of stimulation provided us through the papers and conversations with other molecular beamists. It is our hope that this is only the first of such conferences and that it may be possible to hold one annually.

7. Electric Resonance Voltmeter

Since the inception of the electric resonance method it has probably occurred to a number of people that an electric resonance apparatus might be used as a high precision voltmeter or voltage standard because the frequency of a Stark line is directly dependent on the field strength of the homogeneous field in which the transitions occur. But it has seemed like a pretty complicated way to measure voltage and no one seems to have given the matter any serious thought. However, the techniques of using molecular beams have advanced so far now (mostly through the contributions made by Zacharias at M.I.T.) that it appears that the development of a useful electric resonance voltmeter may be a matter of practical concern. The basis for and possibilities of such an instrument will now be briefly discussed.
A prime requisite of a voltmeter or of a voltage standard is stability and it is this question which will be examined first. In our molecular beam electric resonance apparatus the frequencies of observed lines depend on the particular molecule selected and on the electric field strength in the homogeneous field (C-field). The techniques of frequency measurement and stabilization have reached a very high level of development so that through the stabilization of the transition frequency it should be possible to stabilize to a high degree of precision the electric field strength of the C-field. This field is obtained by the application of some sort of electromotive force to the plates of the field, so that the field \( E \) is related to the voltage \( V \) on the parallel plates of the C-field by

\[
E = \frac{V}{d}
\]

where \( d \) is the separation of the plates. Thus the stability of \( V \) depends on the stability of \( d \) as well as the frequency stability.

To get some idea of the order of stability to be expected let us consider a particular example. In CsF the Stark frequency is about 1200 mc/sec when the electric field strength is 1700 volts/cm. If the transition region is 100 cm long, the spectral line on which the apparatus would be set would have a width of about 1 ke/sec. It should be possible to stay within about 250 cps of the line peak. This means that in terms of frequencies the stability is about 1 part in 5 million. Frequency standards now exist with a stability greater than this. However, the frequency varies approximately as the square of the field strength so that in terms of the field strength the stability is 1 part in 10 million.

To achieve this same stability in the voltage across the C-field plates the plate separation must be this stable. If this separation is 1 cm, then it must stay constant to better than 10 Angstrom units, or better than 1/500 of a wavelength of visible light. This is a stringent requirement and may not be easily met.
Although no instrument now exists which is capable of achieving this stability the specifications mentioned above seen to be realistic in the light of what we now know about the electric resonance method and about molecular beam techniques in general.

Given an instrument that has a voltage stability of 1 part in 10 million, what possible uses does it have? The following uses can be visualized:

1. Standard "cell"

   This instrument like the ordinary chemical standard cell has characteristics which are determined by a natural process. Like the standard cell it would require calibration, and be a secondary standard of voltage.

2. Primary voltage standard

   If the precision obtainable with this instrument surpasses that of existing techniques of voltage measurement, then the possibility exists of making it a primary standard of voltage.

3. Potentiometer

   If a voltage divider is added to the stabilized voltage output of the instrument it can be used for measuring unknown voltages; i.e., it becomes a potentiometer.

4. Voltage stabilizer

   It could be used to stabilize some external source of voltage.

The very high resistance which is available in the electric resonance instrument is a feature which may be very attractive for some applications. It is difficult to estimate this resistance at present, but it would be the resistance between two insulated parallel plates separated, in the above example, by 1 cm.

I have been able to imagine two possible users of an instrument with this precision: namely, the Bureau of Standards, and experimenters whose
apparatus for measuring fundamental constants requires a very stable voltage source.

It should be pointed out that an instrument operated on almost the same principles as that outlined above could be made using the methods of microwave absorption applied to a molecular beam. The difference in the two methods would lie in the method of detecting resonances, the microwave absorption method detecting the effect on the radiation, the present method detecting the effect on the beam. It is likely that a much smaller beam intensity could be used in the instrument discussed above and this may be an advantage in some applications.

Respectfully submitted-
J. W. Trischka
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