

VIBRATIONAL-ROTATIONAL SPECTRA

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I am indeed most pleased to have been invited again to give an Introductory General Lecture before the European Congress of Molecular Spectroscopy. The programme shows that we can expect to hear a whole series of excellent introductory lectures in the separate areas into which the conference has been divided. I shall not, therefore, attempt any sort of comprehensive review of what has been done in the area of rotational-vibrational spectra, but shall instead discuss certain selected topics which happen to interest me particularly and in some of which I can report, in a summary fashion, unpublished work from the group at Harvard. In this way, I believe that I shall overlap the least with the other speakers.

DETERMINATION OF MOLECULAR STRUCTURE

It is customary in talks of this kind to point out the great progress which has been made in a given area since the last conference. However, I fear that my first topic has, in a certain sense, gone backwards in recent years. I refer to the accurate determination of molecular structure from rotation-vibration, or pure rotation, spectroscopy. I believe that the last few years have led to a realization among most workers in the field that we have been unduly optimistic in many of our estimates of the accuracy with which molecular structures can now be determined from microwave spectroscopy or high resolution infra-red or Raman spectroscopy. The reason is well-known to everyone, and is that we do not yet have an adequate method for taking care of the effects of the vibration of the molecule. In principle this is simple: one determines the moments of inertia of a sufficient number of isotopic forms of the molecule in the necessary number of vibrational states so that these moments of inertia can be extrapolated to the vibrationless equilibrium state. This has been done from infra-red spectroscopy for a few very simple molecules. However, chemists are not satisfied to be restricted to simple diatomic and linear molecules. When one proceeds to molecules with more atoms, the complexity of obtaining the necessary data by studying many vibrational states becomes quite overwhelming. The rotational spectra of large molecules cannot be adequately resolved by infra-red spectroscopy, and, further, infra-red spectroscopy usually requires rather pure separated isotopic species if the analysis is to be practical. For these reasons, most spectroscopic determinations of molecular structure have been carried out by pure rotational microwave spectroscopy, which does not normally require separated isotopic species, and which has sufficient resolving power for the larger molecules. But this technique is limited to the low-lying vibrational states which have a reasonable population at convenient temperatures, and we are not, therefore, able to acquire sufficient data concerning

that is really physically reasonable. After we had begun this work, electron diffraction and nuclear magnetic resonance work by Richert and Glemser⁸ and others came to the same structure, but the microwave determination is completely unambiguous.

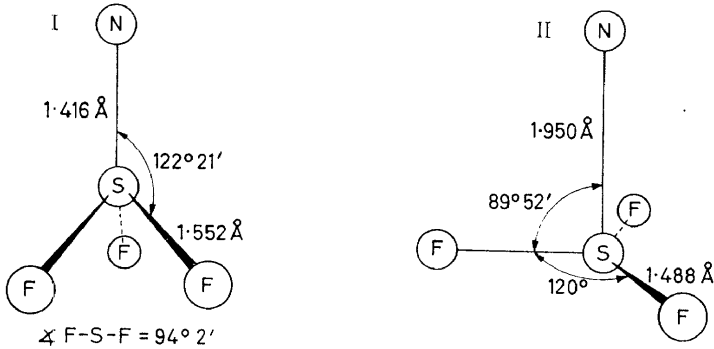
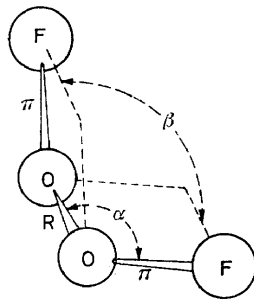


Figure 2. Calculated structures of the NSF_3 molecule

$$\begin{aligned} \mu &= 1.91 \pm 0.04D \\ \text{eq}Q(^{14}\text{N}) &= +1.19 \pm 0.05\text{Mc} \end{aligned}$$

Dr Robert Jackson at Harvard is presently studying O_2F_2 . This is interesting not only because of its structure, shown in *Figure 3*, and its relation to F_2O , F_2O_3 and F_2O_4 , but also technically because it has no life-time at room temperature and not a very great one in our wave-guide at “dry-ice”

Figure 3. Conformation of the O_2F_2 molecule



temperature. However, by flowing the gas through a completely cooled system, it is possible to get perfectly good microwave spectra. Dr Jackson has so far studied the normal isotopic species and the one which contains one ^{18}O atom per molecule. The most interesting feature of this structure is the dihedral angle, α in *Figure 3*. This turns out to be about 87° , whereas the OOF angle is approximately tetrahedral. This dihedral angle is very close to that which has been accepted earlier for hydrogen peroxide, although I have heard rumours recently that vibration-rotation spectra are leading to

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quite a different angle. The microwave vibrational satellite spectra of O_2F_2 are very interesting and are currently under investigation.

Still another molecule for which a qualitative structure is of interest is CH_2NOH , shown in *Figure 4(a)*. Mr Ira Levine is working on this one, and has so far demonstrated definitely the qualitative structure shown, where the hydrogen is bent away from the CH_2 , instead of the other possible form shown in *Figure 4(b)*.

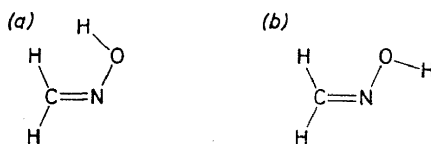


Figure 4. Possible structures of the CH_2NOH molecule

BARRIERS TO INTERNAL ROTATION

Another topic which interests me particularly is that of the measurement and interpretation of barriers to internal rotation. I will not dwell now on the spectroscopic methods^{9,10}, which are not particularly new, except to say that microwave spectroscopy has essentially three different, and more-or-less independent, procedures for the determination of barriers, and that there are also molecules which can be studied through their vibration-rotation interaction in high resolution infra-red spectroscopy. The microwave techniques have now been applied to some dozens of molecules. One development of recent origin is the extension to molecules containing two methyl groups instead of only one. The work of Kasai and Myers¹¹ at Berkeley on dimethyl ether, Swalen and Costain¹² at Ottawa on acetone, Pierce¹³ at Notre Dame on dimethylsilane, and recently Sage¹⁴ at Harvard on *cis*-dimethylethylene oxide, has begun to show what can be done with "two-top" molecules. Of particular interest is the question of whether the interactions between the two "tops" can be accurately extracted from the data. This looks promising but is not yet in a very good state.

In the last few years, there has been not only a continual addition of new experimental values of barriers, but also a steady stream of papers attempting to explain the origin of potential barriers to internal rotation. The prototype molecule for most of these theoretical papers is ethane. It may be of interest to attempt a very brief summary of some of these recent theories. One must start with the pioneer papers of Eyring and his collaborators^{15,16} in the 1930's, because, in fact, there have not been many new ideas introduced that were not at least mentioned in those papers. Thus, he showed that a simple perfect-pairing valence orbital calculation of ethane, with only *s* and *p* orbitals, results in a negligible barrier. Only exchange interactions directly between the hydrogens will contribute anything, because of the cylindrical symmetry resulting from the *sp* character of the bonds (see *Figure 5*). Pauling¹⁷ has recently taken up again the idea that one should put in some *d* and *f* character into the carbon orbitals which form bonds with the hydrogen

atoms. Naturally, this introduction of higher orbitals requires some promotion energy, but, on the other hand, it makes the orbitals more efficient for bonding and, consequently, one would expect that the CH bond would have some *d* and *f* character. Just how much is quite difficult to calculate. The introduction of *d* and *f* character means that the interaction between the carbon orbitals of the CH bonds is no longer cylindrically symmetrical, and one would expect a contribution to the barrier. This is, in essence, Pauling's theory of the origin of the potential in ethane. It has the virtues that it is qualitatively reasonable and that there should not be very much effect on

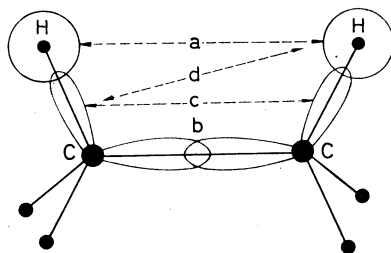


Figure 5. Orbitals and interactions in ethane

the barrier as a result of substituting other atoms for hydrogen. This is what one finds empirically. The difficulty in deciding whether this is indeed an adequate explanation of the barrier is in making reliable numerical calculations. In my opinion, none have been made so far, and, therefore, we must simply say that this is a reasonable idea, with certain appealing features to it, but that we have no idea whatsoever of whether it provides a quantitatively satisfactory estimate of the known barrier.

A second idea, which has been revived recently, is that of imperfect pairing. Only *sp* hybrid orbitals are used, but the next stage of approximation beyond perfect pairing is introduced. This can be described as introducing resonance structures with long bonds in all of the possible ways using only the lowest orbitals. A number of people have explored this idea with contradictory results. Harris and Harris¹⁸ made a very elaborate machine calculation which led to a numerical barrier in the right range. Unfortunately, it is not possible from this work to decide in what way the imperfect pairing caused the barrier. This is a great disadvantage. Furthermore, a somewhat similar but less elaborate calculation, carried out by Martin Karplus¹⁹, led to the opposite result that imperfect pairing did not provide enough energy difference. Hecht and Eyring²⁰ have used this idea in a third way. It had been suggested by several people that the spin-spin coupling constant is a measure of the extent of imperfect pairing. Hecht and Eyring have carried this calculation through using various approximations which lead to a formula relating the barrier in ethane to the hydrogen-hydrogen spin-spin coupling constant for several values of the internal rotation angle. It is unfortunate that they were forced to guess some of these spin-spin coupling constants, since on ethane itself one observes only the value averaged over the internal motion. They admit that the calculated barrier is extremely sensi-

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tive to the numerical spin-spin coupling constants which are used. I am, therefore, forced to conclude that, in the absence of firm experimental values of these constants, they have not demonstrated that this is indeed the origin of the barrier.

There have been still other recent attempts to explain barriers, and one special feature common to most of them has been that the authors come out with the right answer. Unfortunately, at least several of these explanations are additive, so that if we accept the validity of all of them we should come out with a barrier in the neighbourhood of 10 to 15 kcal, since each author has asserted that his own particular explanation is valid and they must all be added together to get the total effect. I fear that we shall have to wait for further work before we will have an adequate explanation of the true origin of these potential barriers to internal rotation.

BENT BONDS

Some very interesting results have been reported, in a preliminary way, on the status of the idea of bent bonds by the group at Berkeley, Flygare, Narath and Gwinn²¹. They have greatly increased the resolving power and accuracy of their microwave spectrograph by electronic stabilization of the Klystron frequency. This has led to greater resolution than has hitherto been easy to achieve. They have utilized this equipment to study 1, 1-dichlorocyclopropane. They report that the quadrupole fine structure in the microwave spectrum which they have analysed shows that the principal axis of the quadrupole tensor for a chlorine atom does not deviate by more than 15' of angle from the geometric carbon-chlorine line. This they interpret as very strong evidence against the idea of bent bonds, at least in these carbon-chlorine bonds. The concept of bent bonds was developed first for cyclopropane, where the internal and external angles cannot be accounted for by ordinary hybridization theory. Of course, it could be that the carbon-carbon bonds are strongly bent, but it does indeed seem strange that there is no evidence of bending in the carbon-chlorine bonds. This appears to be a very important result. It is an unusual result in that, so often when more accurate experiments are made, simple theories break down and need to be replaced by more complicated ones, whereas this result seems in some ways to be simpler than one would have expected.

DEVIATIONS FROM PLANARITY

Another area in which progress has been made is in the study of small deviations from planarity. There have been long arguments about whether certain small ring compounds are truly planar or not. For example, it has been claimed that the rings in both cyclopentane and cyclobutane are not planar. It is very difficult to decide in a simple manner, because of the large amplitude of the out-of-plane vibrations. Recently, there have been several contributions to this subject. Costain and Dowling²² studied the molecule formamide and decided that the molecule was slightly non-planar. Perhaps the most extensive investigations are those of Chan, Zinn and Gwinn²³ on trimethylethene oxide, which has just been published. They studied not

only the moments of inertia but also the Stark effect of certain lines, the relative intensity of vibrational satellite lines due to a ring-puckering vibration, and the vibration-rotation interaction associated with this ring-puckering motion. These all provide clues as to the nature of any non-planarity. Their conclusion was that, although the ring was essentially planar, it did have a very small potential maximum at the planar configuration; in other words, the equilibrium configuration was not exactly planar, but the potential barrier for passing through the plane was less than the zero-point energy of the out-of-plane vibration.

Dr Dixon³ made a careful study of the possibility of non-planarity in the

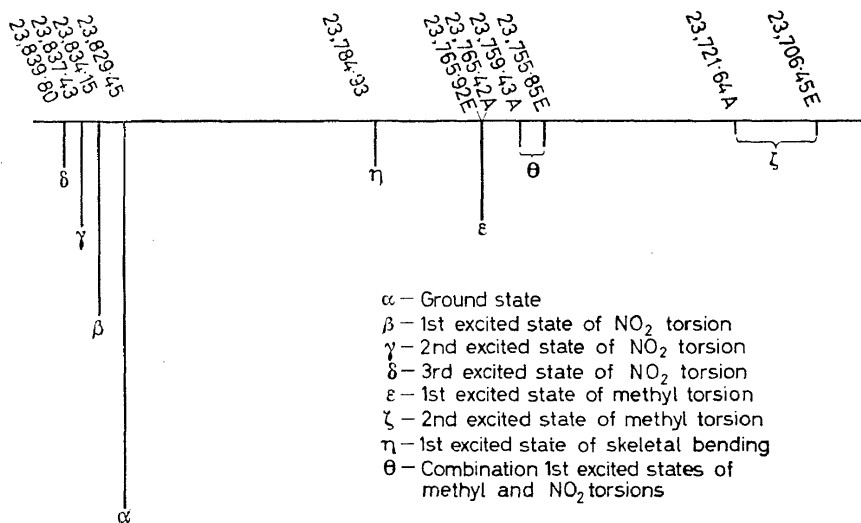


Figure 6. Satellites in the $2_{02} \rightarrow 3_{03}$ transition of methyl nitrate

framework of the methyl nitrate molecule. Figure 1 shows the qualitative structure. We felt that it was possible here to demonstrate that the nitrate group and the methyl carbon are quite accurately in a plane. Three out-of-plane vibrations are expected, one being the methyl group torsion which does not concern us here, one being the torsion about the oxygen-nitrogen bond, and the other being the out-of-plane bending of the two oxygens at the end. We asked whether either of these latter two motions might have a potential maximum at the planar position. Two cases might arise: in one there is a small potential barrier forcing the molecule out of the plane, but so small that rapid tunnelling takes place through it; in the other case, the non-planarity is more severe, with a sufficiently high barrier so that tunnelling is not important. We felt that the latter situation was ruled out rather strictly by the observation on the singly-deuterated molecule. If the molecule were non-planar, even if only bent 1° , there should have been three species, and, therefore, three spectra observed for the three different positions of the deuterium in the methyl group; in fact, only two were observed, as would be expected for a planar symmetry. Next, let us suppose that there is a barrier

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with respect to twisting out of the plane, but that this barrier is so small that tunnelling through it occurs. Then, the satellite spectra shown in *Figure 6* would have been expected to look somewhat different. You can see that, in the limit of a high barrier, these satellites should come together in pairs corresponding to the degenerate pairs of levels produced by the double minimum. We see no evidence here of pairing, either with respect to the position of the lines or with respect to their relative intensities. Finally, we were not able to rule out as rigorously the possibility that there was some non-planarity in the co-ordinate of the bending motion. We saw no satellites arising from this motion, and we think that there would have been some because a potential barrier would have pulled down the first excited state. We summarize this topic by saying that, in many circumstances, there are now quite delicate tests for non-planarity, and quite delicate indications of the nature of any potential barriers which may exist.

ROTATIONAL ISOMERS

A great deal of work over a long period has gone into the study of the rotational isomers of substituted ethanes. Many workers, and especially Professor Mizushima²⁴ of Tokyo and his students, have used infra-red spectroscopy, Raman spectroscopy, electron diffraction and measurements of dipole moments to demonstrate that molecules such as n-propyl chloride exist in two forms, which they call the *trans*- and *gauche*-forms, shown in *Figure 7*.

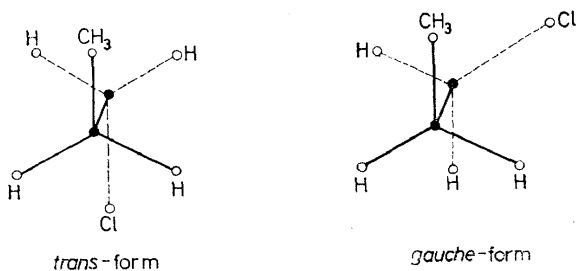


Figure 7. *trans*- and *gauche*-forms, illustrated by n-propyl chloride

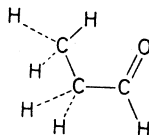
Many measurements of the relative energies of the *trans*- and *gauche*-forms have been made and usually the *trans*-form is more stable, but not always.

In 1957, Mukhtarov²⁵ in Russia published a report on the microwave spectrum of 1-chloro-2-fluoroethane, in which he demonstrated that the *gauche*-form was present. He also determined the dihedral angle to be about 70° . The dipole moment of the *trans*-form was presumably too low, so that no spectra for that form were reported. This year, Dr Eizi Hirota, who is visiting our laboratory at Harvard, has been working on the microwave spectrum of n-propyl fluoride. He has demonstrated conclusively that this molecule does exist in both the *trans*- and *gauche*-forms. By measuring relative intensities he has found the difference in energy to be about 400 cal/mole favouring the *gauche*-form. This is not surprising, as the propyl halides have been studied before by other methods and the *gauche*-form found to be more stable.

It is most interesting to me that Dr Hirota has been able to determine the barrier to internal rotation of the methyl group in both forms. The values are nearly identical: ~ 2.7 kcal/mole. There is more to be learned from these spectra and, particularly, it is just possible that enough information is obtainable to give a potential function for the rotation about the other carbon-carbon bond. In fact, Dr Hirota has some preliminary results on this.

Another molecule which has been found to demonstrate rotational isomers through its microwave spectrum is propionaldehyde. Mr Samuel

Figure 8. Structure of *cis*-conformation of propionaldehyde



Butcher observed and identified transitions which he can show to be due to a *cis*-conformation of this molecule, shown in *Figure 8*. In addition, he has identified transitions from another rotational isomer which he believes to be an out-of-plane form which might well be twisted by roughly 120° around the single bond. So far, he has obtained the barrier only for the *cis*-form, with a result of 2.7 kcal/mole. The indications are from the intensity that the *cis*-form is the more abundant, but this is not certain. On the other hand, nuclear magnetic resonance work of Abraham and Pople²⁶ has recently appeared in which they also find a *cis*-conformation and claim that it is the more stable of the two.

I think that we can now look forward to studying many of these rotational isomers with new precision and with new types of information. I shall return to this topic very shortly.

THE STUDY OF NON-BONDED FORCES

Although I am not convinced that any of the theories so far proposed for the origin of the ethane barrier is yet convincingly proven, this does not stop us from using the values of methyl group barriers and conformations to learn something about other forces within molecules. *Figure 9* shows the results of the measurement of potential barriers to internal rotation of the methyl group in four compounds related to propylene. Lide and Mann²⁷ obtained 2.0 kcal/mole for propylene, Siegel²⁸ found 2.2 kcal/mole for the *trans*-fluoropropylene, and Pierce and O'Reilly²⁹ 2.4 kcal/mole for the adjacent fluoropropylene, and last year Beaudet³⁰ studied the *cis*-form with a rather startling result of 1 kcal/mole. The situation may be strictly analogous to that found a long time ago from thermodynamic data for *cis*- and *trans*-butene-2, which are molecules in which the fluorine has been replaced by methyl. The *trans*-compound shows about 2 kcal/mole and the *cis*-form only 0.4 kcal/mole. Pitzer³¹ explained this as a simple question of steric hindrance between the hydrogens. The equilibrium conformation of the methyl group in propylene has been measured by Herschbach and Krisher³², and found to be the same as in all other compounds with a double bond, namely, as shown

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in *Figure 10*, with the one hydrogen in the plane of the double bond and nearest to it. Hence, hydrogens would interfere more strongly in the equilibrium conformation in the *cis*-isomer, thus pushing up the bottom of the barrier potential function. In the non-equilibrium conformation, they would be farther apart, and thus would alter the top of the potential barrier by a smaller amount. The net effect of this repulsion would, therefore, be to diminish the barrier. Since the thermochemical measurements of Kistiakowsky *et al.*³³ showed that the *trans*-form of butene-2 is more stable than the *cis*-form by about a kcal/mole, this explanation of the barrier change seems quite reasonable. Unfortunately, in the case of fluoropropylene, there are strong but not completely conclusive arguments that the *cis*-form is the more stable. In fact, in simple *cis-trans* isomers, it seems that most often it is the *cis*-form which is the more stable. It may be possible to reconcile a steric repulsion theory of the lowering of the barrier with this greater stability for the *cis*-form, but it may be that an attractive theory is the correct one. The attractive force law is probably a good deal less steep than the repulsive law, and, if it

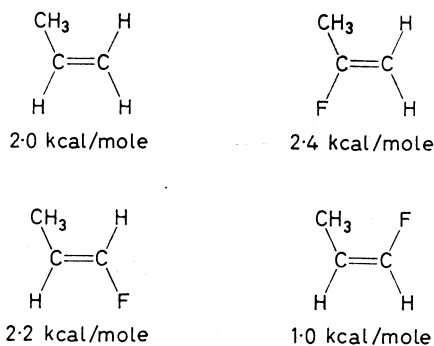


Figure 9. Barriers for the fluoropropylenes

is sufficiently less steep, then the fact that in the non-equilibrium conformation there are two hydrogens in the position of being nearest instead of one may dominate. The fact that they are farther away may be overcome by the fact that there are two of them. This will never be true in a repulsive theory, because of the extremely steep force law. Beaudet is attempting to clarify this situation by studying chloropropylene. He has obtained the barrier in the *trans*-form which is very near to that of propylene, but he has not yet succeeded in completing his analysis of the *cis*-form.

This leads us back to a further consideration of the *trans-gauche* rotational isomers I mentioned earlier. For example, in *n*-propyl fluoride, I pointed out that it is known that the *gauche*-form is the more stable. This certainly sounds like attraction, as has been claimed before by Szasz³⁴. However, in this case, there is apparently no effect on the methyl barrier. The *trans*- and *gauche*-forms have nearly the same methyl barrier. The distances are slightly greater and this may be the explanation, but the state of affairs at the present moment is somewhat unsatisfactory.

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Furthermore, in propionaldehyde the *cis*-conformation is the preferred one about the other carbon-carbon single bond. Eventually, we hope to have the barriers for both conformations.

I very much hope that some of these finer details which microwave spectroscopy can now reveal, and particularly the differences in energy,

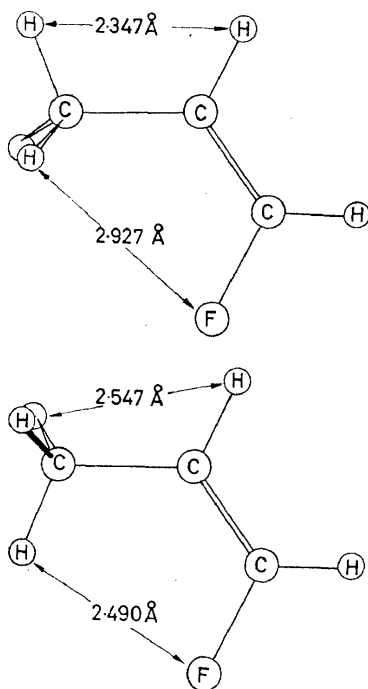


Figure 10. Conformations of *cis*-1-fluoropropylene

structure and barrier for different rotational conformations, will ultimately lead us to a much better understanding of non-bonded forces. I certainly am extremely dissatisfied with the formulae for intramolecular forces which exist in the literature. There are many such formulae, and they differ one from another quite markedly. When the evidence on which they are based is examined, it does not seem to be very good.

I shall conclude by apologizing for not covering many other topics in this general area which undoubtedly are of equal importance to those I have mentioned; on the other hand, I thought it would be better to talk about some of the work with which I am familiar. I hope that I have convinced you that there are many new worlds left to conquer and many fields of application yet to be fully exploited by high resolution, vibration-rotation and pure rotational spectroscopy.

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