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ON THE PERSISTENCE OF MOLECULAR ROTATION AND VIBRATION IN COLLISION

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Abstract

The present paper attempts to explain some observations on the exchange of vibrational and rotational energy of molecules on the basis of the laws of impact, taking into account the postulate of quantisation. It is pointed out that when one of the bodies involved in the impact is much lighter than the other the exchange of energy becomes improbable. The persistence of rotation of HgH molecules in an excess of nitrogen, suggested by Beutler and Rabinowitsch, is discussed. A related phenomenon is found in some chemical activations produced by H_2 molecules but not by any other molecule. The resonance rule for the probability of impacts of the second kind needs some modification for the exchange of vibrational and rotational energy between molecules. The transfer of vibration and rotation from the excited iodine molecule is discussed. In electron impact, the rotation of the molecule does not change, but the vibration does. This is interpreted on the basis of a hypothesis introduced by Franck and Jordan. Within ordinary gases, N_2 or H_2 or I_2, no persistence of vibration or rotation should be expected.

In THE present paper, an attempt is made to explain some observations, concerning molecular vibration and rotation from a classical standpoint, taking into account the postulate of quantisation. It should be emphasized, that this treatment of impact is intended to serve only as an approximate picture which may be of value as a starting point for experimental work.

I. Rotation of HgH in N_2

In a recent paper, Beutler and Rabinowitsch[1] offer an interesting interpretation of an experiment carried out several years ago by Wood and Gaviola.[2] These authors investigated the "sensitized fluorescence radiation" of Hg vapor with the addition of very little hydrogen and a considerable amount of nitrogen. Exciting the mercury atoms, they observed in fluorescence the band spectrum of the HgH molecule. It is a strange fact that the intensity distribution within the individual band corresponds approximately to a temperature of 3000°K, although the experiment is carried out at room temperature.

In a thorough discussion, Beutler and Rabinowitsch come to the conclusion that the excited HgH molecules are produced in the following two steps. The first elementary process consists of the exchange reaction $Hg' + H_2 = HgH + H$. In this reaction the 0.62 volt excess atomic energy over the required chemical energy changes partly into rotational energy of the HgH molecule, thus producing a rotation far exceeding the normal value. In a

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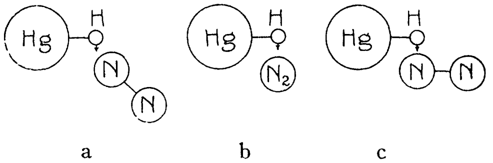
[1] H. Beutler und E. Rabinowitsch, Zeits. f. Physik. Chem. (B) **8**, 403 (1930).

[2] E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1191 (1928).

later process, this HgH molecule is excited by an impact of the second kind with another excited mercury atom. There are, however, only a very few of these excited mercury atoms. Therefore the authors assume that the anomalous rotation of the molecule HgH, produced in the first process, persists until the HgH collides with an excited Hg atom, in spite of a great many (more than 1000) collisions, most of them with N_2 molecules. It is possible of course, that the HgH molecule is formed with a still higher energy of rotation and gives part of it away. At any rate it is unexpected that the great number of intermediate collisions should fail to reduce the rotational energy to the normal value before the excitation of the molecule takes place. Are we able to understand this apparent persistence of rotational energy by the laws of impact?

An essential feature of the experiment is the heavy molecule HgH, having but a small moment of inertia, colliding with the molecule N_2, which is heavy compared with the H-atom. A reasonable picture of the collision is that the HgH molecule consists of the heavy mercury atom at rest and the H atom revolving about it with highest speed because of its small weight and the abnormal rotation produced by the excess energy of the reaction. This system collides with the N_2 molecule, supposed to be comparatively slow and not rotating. This impact is evidently related to the ordinary impact between a light and a heavy particle: the light particle is unable to give away any considerable fraction of its energy on account of the laws of impact.[3] In collision, the rotational energy and the moment of momentum given up by the HgH, split up generally into two parts, one of them going over into *rotation* of the N_2, the other into *translation* of the N_2, knocked away from the heavy system HgH in the direction of the arrow (Fig. 1a).



a b c

Fig. 1. Transfer of rotational energy of HgH to N_2

Since the general discussion of this collision is complicated, it will be sufficient to treat two extreme cases. First, we assume that the fast H atom in its circular orbit collides in a head-on collision (Fig. 1b) with a rigid body, representing the N_2 molecule. Thus from classical mechanics, we come to the result that the H atom is able to give away 1/7.5 of its energy (or less if the collision is not head on).

Let us next consider the other extreme case, in which the rotational energy of the HgH goes over as much as possible into *rotational* energy of the N_2 molecule (Fig. 1c). The fast H atom hits the left N atom, while moving toward its nucleus and perpendicular to the nuclear axis of the N_2 molecule. This col-

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[3] Cf. J. Franck, Zeits. f. Physik **25**, 312 (1924) and G. Joos und H. Kulenkampff, Phys. Zeits. **25**, 257 (1924).

lision accelerates the left N atom in a direction, in which it can move an infinitely small distance, without accelerating the right N atom. Therefore, we are allowed to compute the resulting motion of the whole N_2 molecule in two separate steps. In the first step, only the left N atom is accelerated by the fast H atom; and after the collision, in the other step, the kinetic energy of this N atom produces such a translation of the whole N_2 molecule that its center of gravity keeps its velocity constant and in addition the molecule starts its rotation. The result is that the HgH molecule can give away 1/4, or probably less, of its rotational energy. The same reasoning should hold for the persistence of vibrational energy, although no observation of the phenomenon is known.

Since collisions are not head on in general, we understand that the rotational energy of HgH is given away in collision with N_2 molecules only in small steps—or with small probability if only large quanta are available. Thus we understand a persistence over let us say 10 or 20 collisions, but not over many thousand collisions, as suggested by Beutler and Rabinowitsch. This smaller amount of persistence, however, seems to be sufficient, if we assume a slightly different process of excitation. We assume that the metastable atom Hg′ excites a HgH molecule with normal rotation, but with considerable vibration. This type of transition is understood by the Franck-Condon rule. When the H atom, vibrating as a part of the HgH molecule, collides with a comparatively heavy body, e.g., the N_2 molecule, its energy may change easily into its own rotational energy. On account of the laws of impact, the heavy N_2 molecule takes away only a small amount of energy. Thus a HgH molecule is produced with strong rotation which may collide, before it radiates, several times with N_2 without losing much of its rotational energy. When in a mixture of molecules containing light and heavy atoms some light atoms have a preferred energy, the general tendency is that equipartition of energy is reached first among the degrees of freedom of the light particles, much later among the degrees of freedom of the heavier particles. When N_2 is replaced by H_2O, we expect a rapid dissipation of the rotational and vibrational energy of HgH on account of the numerous H atoms present.[4] This explanation differs from that of Beutler and Rabinowitsch in that it assumes a persistence of rotation only during the life-time of the excited state, i.e., over a few collisions, but not over the long period between formation and excitation of the HgH molecule.

2. Relation to Activation Energy

In the present theory, the persistence of vibration and rotation is interpreted not as a fundamental quality of these degrees of freedom, but as due to the special interaction of light and heavy bodies in collision. Therefore it

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[4] Presumably the peculiar intensity distribution in the HgH bands, observed in the electric discharge by W. Kapuscinski and J. E. Eymers (Zeits f. Physik **54**, 252, 1929) is to be explained by the same phenomenon. However, the process of excitation in the electric discharge is not so well understood as in fluorescence; in the discharge, excitation could take place in the same elementary process as the formation of the molecule HgH, contrary to the fluorescence experiment.

should be expected that this persistence plays a part in chemical activation, because it may happen that some molecules are able to give away activation energy, as far as it is vibration or rotation, not to any partner but only to a selected type of molecule.

Professor G. B. Kistiakowsky has pointed out to me, that possibly this type of selection plays a part in the "mono-molecular" decomposition of some organic compounds. From a thorough experimental and theoretical discussion, Hinshelwood[5] has drawn the conclusion that hydrogen, but no other gas, has a special power to activate the vapors of diethylether, dimethylether, propionic aldehyde and acetaldehyde by thermal impact. These organic molecules contain groups of H atoms. It might be assumed that the energy of activation consists largely of vibration of these H atoms. According to the present argument, their vibration should show a persistence in collision with heavier molecules but not with the lightest molecule H_2. This ability to *give away* vibrational energy should correspond, according to the principle of microscopic reversibility, with the ability to *take up* vibration from a colliding H_2 molecule, but not from heavy molecules.

It remains to explain, however, why helium fails to show the same effect, although it has only two times the weight of H_2. As in the interaction between HgH and N_2, we assume again that the vibration of an H atom, belonging to the organic molecule, is excited by ordinary collision with the H_2 molecule or the He atom. Both of them are somewhat heavier bodies which must have a sufficient excess of energy in order to give the energy of vibration to the bound H atom. From the Raman effect this energy level of vibration of the H atom attached to carbon is known[6] to be approximately 3000 cm^{-1}. According to the laws of impact, the H_2 molecule must have 12.5 percent more energy, whereas the He atom must have 69 percent more energy. Assuming a temperature of 520°C as in Hinshelwoods experiments, we come to the conclusion, that the number of H_2 molecules, able to activate, is ten times larger than the corresponding number of He atoms. This ratio, calculated only from the masses of H_2 and He, seems to be not quite sufficient to explain the observed difference. It should be taken into account, however, that the H_2 molecule with its five or six degrees of freedom contains on the average much more total energy than the He atom with its three degrees of freedom.

3. Probability Rule for Impacts of the Second Kind

On the basis of a group of experiments, Frank and Jordan[7] have established the general rule that in impacts of the second kind most probably the smallest possible amount of energy of *translation* is produced. Kallmann and London[8] derived the same rule from wave mechanics, describing the transfer

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[5] C. N. Hinshelwood, Proc. Roy. Soc. **A114,** 84 (1927) and C. N. Hinshelwood and P. I. Askey, Proc. Roy. Soc. **115,** 215 (1927) and **116,** 163 (1927).

[6] D. H. Andrews, Phys. Rev. **36,** 549 (1930).

[7] Cf. J. Franck und P. Jordan, Anregung von Quantensprüngen durch Stösse, Berlin 1926, p. 226.

[8] H. Kallmann und F. London. Zeits. f. physik. Chem. (B) **2,** 207 (1929).

of excitation energy by a resonance phenomenon without introducing the translation in their equations explicitly. Corresponding to this rule, Beutler and Rabinowitsch discussed the persistence of rotation assuming that the rotational energy of HgH should change in collision mainly into *rotational* energy of N_2, only the smallest possible fraction going over into energy of *translation.*

Franck and Jordan based their rule on experiments in which the initial state of the energy is represented by an excited *electronic level.* It is doubtful if this rule applies without modification to the exchange of vibrational and rotational energy between molecules. However, this exchange can be represented to some extent by classical mechanics.[9] The mechanical treatment of exchange of vibrational and rotational energy between two colliding molecules leads necessarily to the formation of a considerable energy of translation, (cf. Fig. 1c) thus violating the rule that no energy fo translation is produced. Hence the rule seems to apply strictly to a limiting very important case i.e. the exchange of energy between electronic levels.[1] For the motion of heavy masses, however, it requires some modification.

4. ROTATION AND VIBRATION OF I_2 IN HE

Some related phenomena are known. Beutler and Rabinowitsch refer to the iodine fluorescence radiation, excited by monochromatic light and changed, according to the experiment of Franck and Wood,[11] by the addition of helium. This experiment shows a transfer, although a rather slow one, of rotational energy of the iodine molecule. Some persistence of rotational energy is in this case probably due to the large mass of each iodine atom making impossible the transfer of much energy in a single collision with a light Heatom.

Wood and Loomis[12] describe the transfer of *vibrational* energy from I_2 to He, observed in the same experiment. It takes place very seldom, although from the standpoint of mechanics it could take place as well as the transfer of rotational energy.

We may explain the observation that the vibration is affected less than the rotation by taking into account a general distinction between rotation and vibration. The rotational energy is in any moment kinetic energy, where-

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[9] How successful this classical treatment of the nuclear motion is, can be seen in the accomplishments of the theory of intensity distribution in band spectra, based on a mechanical picture by Franck, extended and expressed in wave mechanics by Condon (Proc. Nat. Acad. Sci. **13,** 462 (1927).

[10] If there is kinetic energy of a heavy mass produced—e.g. excitation of Hg going over into vibration of N_2—it should take place indirectly as discussed below, footnote 14.

[11] J. Franck and R. W. Wood, Verh. d. d. phys. Ges. **13,** 78 (1911).

[12] R. W. Wood and F. W. Loomis, Phil. Mag. **6,** 231 (1928). This phenomenon in which the colliding H atom takes up only a small part of the vibrational energy of the heavy I_2 is related to the phenomenon described by Knudsen's "accommodation coefficient" which, in turn, defines the degree to which a reflected gas molecule adjusts its energy to that of the reflecting surface (Ann. d. Physik. **34,** 519 (1911). For Pt and W surfaces this coefficient increases with the molecular weight of the gases.

as in vibration the energy changes continually between the kinetic and potential form. It is available for impact only in the short time interval in which most of it is kinetic and in which the atoms are moving apart. Hence in collisions with a monatomic gas, vibrational energy should show a greater persistence than rotational energy.

In order to explain Wood's and Loomis' observation (the comparatively large persistence of vibration) still another difference between vibration and rotation should be taken into account. Let us consider the inverse process. He atoms of high speed colliding with I_2 molecules, which may be considered to have no appreciable energy. How probable is the transfer of the kinetic energy of the fast He atom into vibration or rotation or translation of the I_2 molecule? For exciting *vibration*, the most favorable direction is along the *line* of the nuclear axis (Fig. 2a). For exciting *rotation*, however, the most favorable direction of the He atom is any direction within the two *planes*, represented by dotted lines in Fig. 2b. Finally, for the transfer of energy of *translation* from the He to the I_2, there is no direction preferred within the whole *spherical angle*. Therefore the chance for translation is larger than for rotation, and this again larger than the chance for vibration. We may conclude, that in the inverse process, where the He atom takes up energy, the vibration of the I_2 molecule should be more persistent than the rotation, in agreement with Wood's and Loomis' observation.

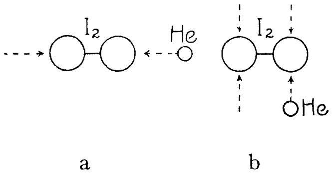

Fig. 2. Excitation of vibration and rotation of the I_2 molecule by the He atom.

5. Excitation of Vibration and Rotation by Electron Impact

Similar considerations may be applied to the excitation of molecular vibration and rotation by electron impact. From his experiments, Harries[13] drew the conclusion, that a 5-volt electron is able to excite *vibration* of the N_2 molecule, but that it cannot excite *rotation* at all. It has been pointed out by Franck and Jordan,[14] that this excitation of vibration cannot be understood by an ordinary elastic collision of the fast electron hitting the molecule head on (Fig. 2a), because the light mass of the electron is not able to give away this large fraction of its energy in elastic collision. The same inability of the electron holds for rotational energy, although the rotational quanta of N_2 are much smaller than the vibrational ones.[15]

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[13] W. Harries, Zeits. f. Physik **42**, 26 (1927).

[14] J. Franck and P. Jordan, Anregung von Quantensprüngen durch Stösse, pp. 255 and 244.

[15] W. Rasetti, Phys. Rev. **34**, 367 (1929); the 5-volt electron giving away 1/1400 of its energy to an N atom, cannot excite the rotational quanta of the N_2 molecule. The same result holds in collision with a H_2 molecule.

Instead of the ordinary elastic collision between the 5-volt electron and the N_2 molecule, Franck and Jordan assume that the approaching electron has some influence by its electric field on the law of force keeping the N atoms together. The main difference between both pictures of collision is the following: in the ordinary elastic collision, the impinging electron would transfer part of its energy and impulse directly into translation or vibration or rotation of the molecule. In the hypothesis of Franck and Jordan, however, the electron penetrates the structure of the molecule. Without exciting a higher electronic level of the molecule—the first level requiring 8 volts—the electron modifies by its field the law of force keeping the atoms together. Thus by its mere presence, the electron may shift the equilibrium position of the nuclei, represented by the minimum of the potential curve. The nuclei start the vibration, accelerated not directly by the impact of the electron, but indirectly by the modified law of force. If the passage of the electron across the molecule takes an appreciable time compared with the period of vibration, it may happen, that the electron leaves the molecule in the vibrating state. From our point of view, the main feature of this hypothesis is, that the acceleration of the nuclei is produced indirectly by the modified law of force. This can give rise only to vibration, not to rotation on account of the conservation of moment of momentum. Therefore in collision with 5-volt electrons, we should expect an energy transfer in vibration only, but a strong persistence of rotation. This conclusion is in full agreement with Harries' experiments.[16]

(It would be hard to introduce the corresponding assumption that in the collision between I_2 and He discussed above, the *neutral* He atom, colliding at room temperature with an energy as low as 0.03 volt, causes an appreciable change in the law of force of the I_2 molecule. In this collision between heavy bodies there is no reason to discard the ordinary mechanical picture of the collision.)

6. EXCHANGE OF VIBRATION AND ROTATION WITHIN ORDINARY GASES

In the examples discussed above, some persistence of vibration or rotation is due to the extreme ratio of masses, e.g. of electrons colliding with N_2 molecules. The most important case consists of collisions within the molecules of the same gas, N_2 or H_2 or I_2. No restriction for the energy transfer and therefore no persistence of the same type should be expected.

Concerning these collisions, there are almost no optical data available.[17]

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[16] The marked resonance in the transfer of excitation of the Hg atom into vibration of N_2 or CO or H_2O (H. Beutler and E. Rabinowitsch, Zeits. f. physik. Chem. B. **8,** 411 (1930) demonstrates that no appreciable translation is produced. Therefore, this process is very different from a mechanical impact, as should be expected because the initial state of the energy, the excited state of the atom, has no kinetic energy of a heavy mass. It should be described by a similar picture as Franck's and Jordan's, i.e., we assume that the close contact with the excited Hg atom modifies the electronic level and therefore the law of force of the molecule and changes the equilibrium position of the nuclei, thus starting vibration. (Cf. H. Beutler and W. Eisenschimmel, Zeits. f. physik. Chem. **10,** 103, 1930.)

[17] The complicated background in Wood's photographs of the resonance series in I_2 with long exposure (Phil. Mag. **35,** Plate VI, f. 1918) should be due to this process.

Professor A. Eucken called my attention to the fact, that we may draw a conclusion from thermal measurements. It is consistent with our expectation that the ratio of specific heats, measured from the velocity of sound, does not change at the highest frequencies[18] which means that, even for the quickest change of temperature, equipartition is maintained among all degrees of freedom of the diatomic molecule. It should be concluded that vibration and rotation are taking their full share in the exchange of energy. The great experimental difficulty, however, in these experiments should be emphasized.

The classical treatment of impact applied in the present paper is intended to serve only as an approximate picture which may be good as a starting point for experiments. An experimental investigation is under way. A more thorough treatment of these processes on the basis of wave mechanics is being developed by Dr. C. Zener. Some interesting results, published recently by R. Rompe[19] lead to the conclusion that some specific influence of the electronic term takes place. This kind of influence does not lend itself to representation by a classical picture.

Our main conclusion is that the persistence of vibration and rotation can be explained largely by classical ideas. Especially in the complicated interpretation of the HgH fluorescence given by Beutler and Rabinowitsch, the most doubtful detail, i.e., the excitation of abnormally rotating molecules, is understood by a general rule, the equipartition of energy being reached at a rate depending largely on the ratio of the weights of the particles. This result supports the other steps of the interpretation given by Beutler and Rabinowitsch which are of importance in photochemistry.

The author greatly appreciates the criticisms of Professor J. Franck, Professor E. C. Kemble and Dr. C. Zener.

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[18] C. D. Reid, Phys. Rev. **35**, 814 (1930) and M. Grabau, to be published in spring 1931.

[19] R. Rompe, Zeits. f. Physik **65**, 425 (1930).