production by the (n,α) reaction, since the (n,γ) cross section[8] of Li^7 is only 0.03 barn and that[9] of Li^6 in the

[8] See reference 7, p. 4.

[9] B. Hamermesh and V. Hummel, Argonne National Laboratory (private communication).

natural element is less than 0.1 barn. Since boron, lithium, and deuterium are all $1/v$ absorbers, the cross section of deuterium for 2200-m/sec neutrons can be calculated to be 0.57 ± 0.01 millibarn.

Resonance in Collision Processes*

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The limitations are investigated under which "resonance" provides certain collision processes with preferred probability. In impacts of the second kind, resonance strongly affects the transfer of electronic into electronic energy or into a small amount of vibrational energy, possibly the transfer of vibration into vibration, certainly not the transfer of vibration into rotation. Resonance is not effective in the transfer of energy of atomic recombination into electronic energy and, in general, resonance is not effective in processes in which nuclei change positions by appreciable amounts.

I. INTRODUCTION

IN certain cases impacts of the second kind show a preferred probability which Franck has attributed to "resonance." A similar preference due to "resonance" has been claimed for numerous other processes, in some instances with, in others without justification. In particular, certain theories of the afterglow of nitrogen, that is, of "active nitrogen," encounter difficulties by over-emphasizing the principle of resonance which actually applies only to a limited group of processes. The present paper proposes to examine the limits within which this principle is valid.

II. RESONANCE

We consider collision processes in which energy is transferred from one quantized energy level to another in atoms or molecules. Impacts of the second kind are an important type. In certain instances a particularly large probability for the transfer of energy has been observed. Franck[1] described such cases by adopting the principle that the cross section of the process is large *if no energy or only little energy is changed into translation or received from translation*. A striking example of this condition, which is called "resonance," is given by the observation of Beutler and Josephy[2] that excited mercury atoms Hg' transfer energy to Na atoms with a pronounced preference to the Na level with an energy closest to that of Hg'. Fluorescence of Na provides another example. When one of the D lines of Na is separately excited, the other D line appears, depending upon the pressure, presumably excited by impacts of the second kind. Manley and

Duffendack[3] observed resonance in the simultaneous ionization and excitation of magnesium atoms caused by impacts of the second kind with metastable or ionized neon atoms.

The corresponding effect in the energy transfer from an atom, argon, to a diatomic molecule, hydrogen, was observed by Lyman and later interpreted by Dieke and Hopfield.[4] A hypothetical, more extreme process illustrating such cases is the excitation of the O_2 molecule, for which the potential curves are well explored. While the energy of dissociation of O_2 is 5.08 ev, the molecule readily absorbs light of greater energy in a continuous range leading to excited molecules in a state of such compression that the molecule immediately dissociates. There is little doubt that the O_2 molecule may receive the same amount of energy by an impact of the second kind from an atom endowed with, say, 6 ev energy of excitation. Again a preferred probability due to resonance is expected to govern this transfer of electronic energy, irrespective of the fact that ultimately the free atoms produced are given energy of translation.

Mott and Massey[5] discuss the theory of the resonance effect and conclude that the sharpest resonance is expected for transfer of excitation involving optically allowed transitions in both systems.

An additional rule governing the probabilities of impacts of the second kind, derived by Wigner[6] on the

[1] J. Franck and P. Jordan, *Anregung von Quantensprüngen durch Stösse* (Springer, Berlin, 1926), p. 226.

[2] H. Beutler and B. Josephy, Z. Physik 53, 747 (1929). See H. Beutler, Z. Physik 50, 581 (1928).

[3] J. H. Manley and O. S. Duffendack, Phys. Rev. 47, 56 (1935).

[4] T. Lyman, *Spectroscopy of the Extreme Ultraviolet* (Longmans Green, New York, 1928), second edition, p. 91; G. H. Dieke and J. J. Hopfield, Phys. Rev. 30, 414 (1927).

[5] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 284. See P. M. Morse and E. C. G. Stueckelberg, Ann. Physik 9, 579 (1931).

[6] E. Wigner, Gött. Nachr. 375 (1927). For the experimental confirmation, see A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Company, New York, 1934), p. 69.

basis of quantum mechanics, claims a preference for a transfer in which the total resultant electronic spin of the colliding partners remains unchanged.

A process closely related to a collision of the second kind is charge transfer, for example, $He^+ + A \rightarrow He + A^+$. Mott and Massey point out that here again the effective cross section is largest in the case of resonance; that is, if the two partners have nearly equal energies of ionization.[7]

The examples referred to above are concerned with the transition of *electronic* into *electronic* energy. For the conversion of *electronic* energy of Hg into a *vibrational* quantum in various molecules, Zemansky[8] found relations which again are well described by resonance (although with an exception).

Less clear-cut is the problem of the transfer of energy of *vibration* to *vibration*. We compare this process with the excitation of vibration by electron impact. The application of the primitive picture of a fast electron hitting a diatomic molecule along the internuclear line leads to the prediction that the electron, because of its relatively small mass, simply bounces back without exciting vibration. Experiment, however, shows that an electron of a few volts energy is able to excite a vibrational quantum in H_2 or N_2.[9] For this process Franck[10] suggested a special picture in which the impinging electron is supposed to hit the molecule not along its internuclear line but in its equatorial plane. While the electron is crossing the molecule, it affects the internuclear force and so starts the vibration of the molecule. When the electron leaves the molecule, it may happen that the nuclei have just the positions and velocities which enable them to continue the vibration, the energy being supplied by the kinetic energy of the impinging electron.[11] A similar picture may be applied to the transfer of a vibrational quantum from one molecule to that of another. When the field surrounding a vibrating molecule interacts with a nonvibrating molecule, a transfer of a quantum may occur. It is plausible to assume that such a transfer takes place with a larger cross section between polar than between nonpolar molecules. Eucken systematically investigated such transfer processes by measuring the dispersion of sound. From numerous observations he inferred the general rule that a transfer is probable between molecules such as Cl_2 and CO_2 which are able to react

chemically, although the transfer does not constitute a chemical reaction.[12]

III. NON-RESONANCE

It appears that Franck's principle of resonance, requiring a minimum production of energy of translation, is over-emphasized in papers on other types of collisions, in particular triple collisions. This criticism applies to theories of active nitrogen and will now be illustrated by examples.

It is generally agreed that active nitrogen consists of atomic nitrogen which upon recombining liberates sufficient energy to excite atoms and molecules. The first process to be considered is the recombination of two N atoms which in a triple collision give their energy to a molecule N_2:

$$N + N + N_2 \rightarrow N_2 + N_2'.$$
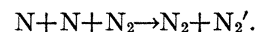
A theory of active nitrogen claims that resonance gives preference to a process in which the total energy of recombination (using the value 7.373 ev) is converted into electronic energy of the third body exciting its level $B^3\Pi_g$, $v = 0$ (energy 7.36 ev). However, one cannot simply apply the theory of Mott and Massey to this triple collision process since the theory applies only to the transfer of *electronic* energy in a two-body collision. There is, however, another theory which demonstrates how readily vibration and translation may be produced in a triple collision. This is the theory of Eyring, Polanyi,[13] and their collaborators describing the triple collision by potential surfaces. It is true that this theory applies only to a simplified case, the approach along a straight line of three atoms, two of which form a molecule in a triple collision. The potential surface shows two valleys between which a transition can be made over a saddle point (representing the activated state). Any transition made by the reacting system is visualized as the free, frictionless motion under gravity of a mass point sliding on the surface. For a triple collision this picture leads to the conclusion that the energy of recombination can well be partly transformed into vibration and translation. This conclusion contradicts the principle of resonance.

When the third body is a diatomic molecule such as N_2, approaching in any direction, the situation is much too complicated to be represented by potential surfaces. Nevertheless, it seems safe to draw the same conclusion that the ready generation of vibrational and translational energy excludes the occurrence of resonance. Since energy of recombination is identical with a limiting case of vibrational energy, the recombination of two atoms in a triple collision rather resembles the

[7] An example is given by an observation of W. Hanle and K. Larché on ionized mercury, Physik. Z. **33**, 884 (1932).

[8] M. Zemansky, Phys. Rev. **36**, 919 (1936). For the theory see L. Nordheim, Z. Physik **36**, 496, 1926; H. Kallmann and F. London, Z. physik Chem. (B) **2**, 207 (1929); K. J. Laidler, J. Chem. Phys. **10**, 34 and 43 (1942).

[9] W. Harries, Z. Physik **42**, 26 (1927); H. Ramien, Z. Physik **70**, 353 (1931).

[10] J. Franck and P. Jordan, *Anregung von Quantensprüngen durch Stösse* (Springer, Berlin, 1926), p. 255.

[11] The theory given by Mott and Massey (reference 5) does not include this case, since it presupposes that the impinging particle hits along the internuclear line.

[12] For reference see O. Oldenberg and A. A. Frost, Chem. Revs. **20**, 99(1937); N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 292.

[13] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 106, Fig. 25.

collision between a highly vibrating molecule and any other molecule. It appears likely that the collision dissipates the mechanical energy, which before the collision is all concentrated in one degree of freedom, distributing it over the various degrees of freedom available—vibrational, rotational, translational and, possibly, electronic. This concept is incompatible with resonance.

This theoretical argument, which implies lack of resonance in atomic recombination, is confirmed by Mohler's[14] observation that the sodium spectrum when excited in active hydrogen by the recombination of two atoms, shows only the D lines and not the higher lines, although resonance between the energy of recombination and the excitation of the atom would bring out several higher lines of the principal series. This observation contrasts with the pronounced resonance discussed above, which is evident in the sodium spectrum when excited by impacts of the second kind with *excited mercury*. The lack of resonance in the same type of triple collision is again evident in the excitation of Hg by active nitrogen, that is, presumably by a pair of recombining N atoms. Here, according to Okubo and Hamada and Bay and Steiner,[15] nearly the total energy of recombination may be transferred to the Hg atoms, but the highest spectral lines produced show only very low intensities, contrary to the prediction of resonance theory. It seems safe to conclude that resonance does not govern the transfer of energy from a recombining pair of atoms to a third body.

Even a physicist who insists on resonance has little reason to predict that the conversion of the energy of recombination of N+N into electronic energy of N_2 will occur with high probability, because this process would imply that the *total* energy of recombination of N+N is transferred to the third body. The colliding pair has many quantized vibrational levels at its disposal to which it may go while making available only a *fraction* of the recombination energy. The energy change from a pair of separate atoms to a nonvibrating molecule has no particular distinction in the large number of possible vibrational transitions, except that it is listed in tables as the energy of recombination of N+N. Therefore, even the argument based on resonance would not lead to a preference for transferring the total recombination energy at once.

Whereas the case just discussed is so complicated that potential curves cannot be drawn, the much simpler case of charge neutralization has been discussed in detail by Bates.[16] Bates found that in the process

$$O^- + N_2^+ \rightarrow O' + N_2',$$
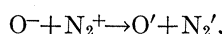
excited levels are produced such that a considerable share of the total energy available is transferred into energy of *translation*. Thus resonance is not effective in this process.

It is of interest to apply the same argument to simple chemical reactions. High probability by resonance is claimed[17] for the exchange reaction,

$$NO + O(^1S) \rightarrow N + O_2,$$
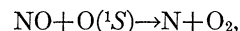
when both products, N and O_2, show certain electronic excitation. However, such reactions are well visualized by potential energy surfaces[18] which show that translation and vibration may readily be produced, thus excluding resonance.

In a chemical reaction, such as the one just mentioned, resonance would imply that the initial partners have the same energy as the final partners; in other words, that the reaction is neither exothermic nor endothermic. There is no chemical evidence in favor of such reactions. On the other hand, there is evidence that a reaction of this type requires an energy of activation. Therefore, reading the reaction in the reverse sense, it is not to be expected that an N atom is able to break up the O_2 structure except when aided by energy of activation, which again would violate the principle of resonance.

Another example is given by the reaction recently suggested by Bates,

$$H + O_3 \rightarrow OH(v=9) + O_2,$$
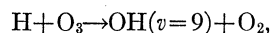
which energetically explains the appearance of OH with a maximum of 9 vibrational quanta. This reaction is of great interest because it explains Meinel's[19] discovery of the corresponding vibrational spectrum in the night glow. Our present argument leads only to the conclusion that $v=9$ is presumably not preferred by resonance but is the maximum obtainable value of vibrational energy stored in the OH radical. However, it would be surprising if in the chemical rearrangement described the total energy available were to go into one degree of freedom, that is, into vibration of OH.

An exchange between *vibrational* and *rotational* energy was studied by Rieke[20] in the spectrum emitted from HgH molecules. He explained the high rotation evident in the spectrum by the original excitation of vibration (governed by the Franck-Condon rule) and the subsequent transfer in collisions of vibrational into rotational energy. In this process the conservation law requires that the angular momentum of the rotation produced by balanced by the angular momentum of the separating particles. Hence here again translational energy is necessarily generated.

Tentatively the results may be summarized as follows: Resonance is important in the transfer of

[14] F. L. Mohler, Phys. Rev. 29, 419 (1927).

[15] J. Okubo and H. Hamada, Phil. Mag. 5, 375 (1928); Z. Bay and W. Steiner, Z. Physik Ch. B, 9, 106 (1930).

[16] Proceedings of the Conference on Ionospheric Physics at Pennsylvania State College (Pennsylvania State College, 1950) p. 12 BB.

[17] J. Kaplan (unpublished).

[18] Reference 13, Fig. 24, p. 105.

[19] A. B. Meinel, Astrophys. J. 112, 120 (1950).

[20] F. F. Rieke, J. Chem. Phys. 4, 513 (1936). See N. D. Smith, Phys. Rev. 49, 345 (1936).

electronic into electronic energy (Hg'+Na) and of electronic energy into a small amount of vibration (Hg'+various molecules). Possibly resonance is important in the transfer of vibration into vibration, but is certainly not important in the transfer of vibration into rotation. The energy of recombination of a colliding pair like N+N is not readily transferred by resonance

to electronic excitation of a third body but more probably is distributed over the various degrees of freedom of the collision complex. Furthermore, in exchange reactions resonance is not effective.

In general, resonance is ineffective in collision processes in which nuclei change positions by appreciable amounts.

Generation of Color Center Precursors in Alkali Halides by Electrolysis

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Two types of imperfections (designated as color center precursors) are created in NaCl crystals when they are subjected to electrolysis. Both of these types are present in a crystal not colored by the electrolysis and lead upon irradiation by x-rays to the development of temporary color centers in much larger numbers than are ordinarily produced and to permanent centers in about the same numbers as result when a crystal is directly colored by electrolysis. In crystals colored directly by electrolysis, only the former type of precursor is present. The properties of crystals containing precursors and of those containing color centers derived from precursors have been studied and compared with those of crystals in the other previously known states. A proposal regarding the nature of the second type of precursor is presented.

I. INTRODUCTION

THE fact that it is possible to produce color centers in ionic crystals is of special interest in the field of solid state physics for essentially two reasons. First, they represent themselves a type of imperfection that is relatively easy to study. Second, it is possible to draw conclusions regarding other types of imperfections through their influence on the tendency of color centers to be formed under the proper circumstances.

Essentially three ways of producing color centers in alkali halides have been reported: irradiation of the crystal with x-rays; exposure of the heated crystal to alkali metal vapors; and electrolysis of the heated crystal (by the use of a pointed cathode and a flat anode). While irradiation with x-rays leads to color centers that are bleached out upon application of light of wavelengths corresponding to one of their absorption bands, the other two methods of coloring lead to permanent color centers which cannot be destroyed by irradiation with light.[1] The formation of color centers is accompanied by changes in other physical properties; for example, it has been reported that the density of CaF_2 decreases upon coloration by electrolysis[2] and the density of KCl decreases upon coloration by irradiation with x-rays.[3] An excess of alkali metal after additive coloring has been observed in NaCl[4] and in KCl.[5]

On the other hand, the extent to which nonpermanent color centers are produced is affected if a crystal undergoes plastic flow before irradiation.[6] Moderate amounts of plastic flow increase the extent to which the crystal is colored by such treatment while large amounts lead to a diminution of the colorability.

We have found that when a crystal is subjected to electrolysis in such a fashion that no coloration is produced, the nature of the color center formation resulting from irradiation by x-rays is altered in the following way. First, the number of nonpermanent color centers is appreciably increased compared to that occurring in a normal crystal irradiated under the same conditions. Second, in addition, permanent color centers are formed, an effect which does not occur when a normal crystal is exposed to x-rays.

It seems reasonable to suppose that this change in the susceptibility for the formation of the two types of color centers is indicative of the presence of new imperfections in the crystal. Reserving for the time being any attempt to specify the nature of these imperfections, we will designate them as color center precursors.[7] There are evidently two types of such precursors, the first kind leading to nonpermanent, the second kind to permanent color centers. The precursors leading to the permanent color centers are metastable in the sense that they persist when the crystal is subjected to heat

[1] See, e.g., P. W. Pohl, Physik. Z. **39**, 36 (1938); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940); F. Seitz, Revs. Modern Phys. **18**, 384 (1946).
[2] E. Mollwo, Gött. Nach. No. **6**, 79 (1934).
[3] Estermann, Leivo, and Stern, Phys. Rev. **75**, 627 (1949).
[4] A. L. Hughes, Revs. Modern Phys. **8**, 294 (1936).
[5] A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 34 (1950).

[6] K. Przibram, Z. Physik **41**, 833 (1927); Burstein, Smith, and Davisson, Phys. Rev. **86**, 615 (1952); for a complete account of the older work see, e.g., F. Seitz, Phys. Rev. **80**, 241 (1950).
[7] Strictly speaking, the vacancy pairs associated with the production of color centers in ordinary crystals are also precursors. We prefer to reserve this term in the present paper, however, for the precursors generated by electrolysis.