DISSOCIATION OF MOLECULES AS DISCLOSED BY BAND-SPECTRA

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The evidence which is furnished by band-spectra in regard to the dissociation of molecules is in essence like that which line-spectra provide concerning the ionization of atoms, for the two phenomena are very similar—so much alike, indeed, that it is suitable for convenience of language as of thought to refer to ionization as a special form of dissociation. In both cases there is, in the limit, separation of the individual particles of a gas—molecules or atoms, as the case may be—into pairs or larger sets of disconnected particles. In both cases there are intermediate steps between the normal state of the undisturbed molecule or atom, and the state of its complete resolution into fragments altogether free from one another.

Total separation may often be detected by physical or chemical means, as for instance when the presence of helium ions in helium gas is shown by electrical experiments, or the presence of hydrogen atoms in molecular hydrogen gas is proved by one or another of the well-known chemical tests for atomic hydrogen. Molecules or atoms in one or another of the intermediate, the so-called *excited*, states may also be detected occasionally by physical or chemical means, as when excited mercury atoms are disclosed by mixing the mercury vapor with hydrogen gas and applying a test for atomic hydrogen, which excited but not normal atoms produce by impact against hydrogen molecules. Many of the phenomena of catalysis, indeed, are probably indications of the presence of excited atoms or molecules.

Line-spectra however furnished the earliest comprehended evidence for the existence of excited states; they still provide the most accurate way of locating these states, and locating the state of ionization. Band-spectra likewise give by far the most accurate way of discovering and locating the intermediate states of a molecule which, so to speak, are steps between its normal unperturbed condition and its complete disaggregation into atoms. It may be superfluous to remark on the importance of such measurements. Even if one were interested only in the attainment of complete dissociation, one could not fail to be instructed by the study of the steps which lead to it; and these steps themselves acquire extreme significance from the fact that in all probability they correspond to various degrees of what is called *activation*. As for complete dissociation, it is discernible from band-spectra as complete ionization is from line-spectra; and here also the accuracy of the spectroscopic method surpasses by far that of any other.

To speak of *locating* excited states or the state of dissociation, or of *accuracy* in measuring them, may give at first a misleading impression. It is not primarily a question of measuring minute quantities of the products of dissociation; rather it is a question of determining the value of energy which on being communicated to the molecule or atom is just sufficient to break it into fragments. The spectra reveal that there is such a critical value of energy, a fact which previously may have seemed reasonable enough but could scarcely have been proved. It is a great advantage of the spectroscopic method, indeed, that the fact of ionization or dissociation, the evidence that it requires a definite minimum amount of energy, and the value of this amount of energy, are all simultaneously furnished by the single spectrum photograph. Much the same thing may be said of the location of excited states. Each is characterized by a definite excess of energy over the energy-value of the molecule or atom in its normal state. To demonstrate an excited state by analysis of a band-spectrum is the last step but one before determining its energy, unless indeed it be the very last step; a complete analysis of any spectrum involves the determination of the energy-values, or, as I shall say, the locations, of all of the excited states and of all of the states of dissociation of the particle which is the carrier of that spectrum. Or, to put the same idea in words slightly different: complete understanding of any spectrum would entail a knowledge of all of the modes of dissociation possible to its carrier, and of all the intermediate steps leading towards these various modes.

Complete knowledge in any field is, however, rare; and it is fortunate that in line-spectra as well as in band-spectra, the lines or the bands—as the case may be—are sometimes so arranged that a particular series of excited states, culminating in a particular mode of dissociation, is almost obvious to even the uninstructed onlooker. The absorption spectrum of cool sodium vapor, for instance, consists of a striking sequence of dark lines. Successive members of this sequence approach more and more closely to one another as one follows the procession from the yellow toward the ultraviolet, until it is evident that they are "converging" upon a limit-frequency which can be estimated with modest accuracy by visual inspection, although the gradual decrease in the distinctness of the lines as they draw towards the convergence point precludes a definite sighting of this latter. The fact that these lines appear in the absorption spectrum of cool unstimulated vapor—that is to say, when the vast majority of the sodium atoms are necessarily in their normal state—shows that each stands for the transition from the normal into some one of the excited states of the sodium atom. The excited states, or more precisely their energy-values, form a converging sequence as the lines form a converging sequence. If I denote by ν_1, ν_2, ν_3, ... the frequencies of the various lines in order of increasing magnitude, and by ν_∞ their convergence-frequency; then the energy-values of the corresponding excited states, relatively to the energy of the normal state taken as zero for reference, are equal to $h\nu_1$, $h\nu_2$, $h\nu_3$ .... ; and the energy corresponding to the limit of the sequence of excited states, referred to the same zero, is equal to $h\nu_\infty$.

Now this limit of the sequence of excited states is the state of ionization; and the energy-value $h\nu_\infty$ is the energy required to effect ionization. It is the so-called *ionizing potential;* but some such term as *heat of ionization* or *work of ionization* is preferable, for the sake of the analogy with dissociation of molecules. For, be it recalled, ionization is that special type of dissociation in which the fragments are a free electron and an atom (or, it might be, a molecule) devoid of one of its normal quota of electrons.

Such a definition evidently contains an element of ambiguity. Though a free electron is presumably a definite object—at least, we have not yet found it necessary to postulate two or more varieties of free electrons—there may well be several kinds of ions. It is conceivable that the sodium atom, deprived of a single electron of its normal quota, might assume any one of a great number of different configurations, each corresponding to a different energy-value, and therefore requiring a different value of work of ionization. In other words there might be many distinct ways of ionizing a sodium atom, each involving the expenditure of a distinct amount of energy, and each resulting in a distinct type of sodium ion.

Such is not only conceivably, but actually, the case. We have only to recall the various types of ionization which give rise to the lines of x-ray spectra, and which are described as extraction of a K-electron, extraction of a L_I electron, and so forth. These are comparatively easy to distinguish from what is commonly called ionization without a qualifying word—detachment of the "loosest" or "valence" electron; for they require much more energy. On passing to the "two-valence-electron" atoms such as calcium, however, we find not only these modes of ionization which involve extraction of inner electrons and high values of ionizing-potential, but also others which lie very close to the minimum ionizing-potentials. Or, to express the facts better, we may say that there is not one, but a group, of low ionizing-potentials. In the optical spectrum of such an element, there are sequences of lines disclosing sequences of excited states which converge upon two distinct energy values, corresponding to two distinct amounts of work of ionization, corresponding to two different states of the positive ion which is one of the two fragments into which the atom is resolved. With elements still farther to the right in the Periodic Table, the multitude of possible and not-very-different ionizing-potentials may be great. This I mention in order to prepare for a fact which is important in the analysis of band-spectra; to wit, that the state of the atoms into which a molecule is resolved by dissociation need not always be the same—that it may be different when the dissociating agency is different—that in particular it need not by any means be the normal state of the atoms in question. Precisely this variability of the fragments resulting from dissociation is one of the most interesting features of the entire field.

Now in the most easily interpreted of the band-spectra—such for instance as that of iodine—a not-too-excellent spectroscope discloses a converging sequence[1] of broad hazy lines. The reason for specifying that the instrument be not too good is simply that with a high resolving power each one of these broad hazy lines—which in fact are *bands*—is discovered to be a rich group of fine lines. Likewise in the case of sodium a good spectroscope reveals that each "line" of the principal sequence or series is in truth a pair of lines. In both cases this "fine-structure" is of the greatest interest and importance; in the former case it reveals the rotations of the molecules. In both cases, however, it is irrelevant to our present interest, at all events for a first examination of our topic; and it is better to ignore the fine-structure of the molecular bands as we have ignored that of the atomic lines, considering each band as a unit as we have considered each sodium line as a unit—that is to say, as the sign of a transition between the normal and an excited state of the molecule. Then the converging series of bands in the absorption spectrum of (say) iodine reveals a converging sequence of excited states of the iodine molecule; and the limit ν_∞ on which they converge, multiplied by h, is the energy-value of the state of dissociation to which this sequence of states leads up—the work of dissociation, of this particular mode of dissociation, reckoned from the normal or initial state of the molecule.

Before entering further into detail concerning these converging sequences, we should consider another sign of dissociation: the presence of a continuous region of absorption extending over a

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[1] I continue to use the word "sequence" for the sake of the analogy with the previous case; but in the technical language of the analysts of band-spectra it has a different meaning.

relatively wide range of the spectrum. In the ideal case—such a case as is approached with sodium—the region of continuous absorption should commence at the convergence frequency of the sequence of absorption lines, and extend thence away from the lines toward higher frequencies. Such a phenomenon in an atomic spectrum would signify that light of any frequency—say ν_s—within this region, is able to extract an electron from the atom, conferring upon it—more properly, upon the system of ion and free electron—kinetic energy of translatory motion in amount $(h\nu_s - h\nu_\infty)$. The region of absorption would be continuous, because there is nothing in quantum-mechanics—so far as we know—to limit kinetic energy of unperiodic translatory motion to discrete "permitted" values.

Now there is a continuous zone of absorption in the spectra of sodium and potassium, lying in the main beyond the convergence-frequency of the principal series; and if we are willing to leave for future explanation the fact that this zone intrudes upon the line-series instead of stopping sharply at its limit, we may assume that it is indeed the sign of ionization with transfer of extra kinetic energy to the separated particles. Likewise, there are continuous zones of absorption in the band-spectra of many molecules, some of which lie around and beyond the convergence-limit of a sequence of bands, while others stretch towards long waves as far as the boundary set by the limitations of the apparatus, so that it cannot be told whether or not they adjoin band-sequences. If we assume that each of these continuous regions of absorption is a sign of dissociation with transfer of extra energy to the separated particles, then in these we have an additional source of evidence for dissociation and even of estimates of the energy required to dissociate.

Suppose then that we have collected and tabulated[2] a number of values of work of dissociation computed either from the short-wave limits of sequences of bands or sequences of excited states, or from the long-wave limits of continuous regions of absorption; can we obtain some independent confirmation of these values?

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[2] Compare such a tabulation in the article of H. Sponer (Ergebnisse exakt. Naturwiss. **6**, 75–103 (1927))

The obvious step is to compare them with the values of work of dissociation—under these circumstances more often called *heat of dissociation*—obtained by conventional thermal methods. We then discover, first, that the best of the values deduced from the analysis of spectra—taking it for granted, of course, that the work of dissociation is truly the product of h into the convergence-frequency of a sequence—are determined with much greater accuracy than the thermal methods are capable of giving.[3] To take one instance only, but the most important; there is no other estimate of the heat of dissociation of molecular hydrogen for which anywhere nearly so small a numerical uncertainty is claimed as for the value—good at least to two per cent—deduced from analysis of the band-spectrum of hydrogen gas. We cannot therefore compare pairs of values of presumptively equal exactness; there is a relatively wide range about any accepted "direct" value, anywhere within which the "spectroscopic" value may be without compelling us to concede a disagreement.

Nevertheless there are cases in which actual undeniable disagreement occurs; and it is most important to observe, that out of these disagreements we infer the principle already stated—that the mode of dissociation effected by light need not immediately result in the formation of two *normal* atoms. What the thermal methods yield, in fact, is the net amount of energy expended upon the gas in the course of transforming its molecules completely into pairs (for simplicity I am speaking as though all molecules were diatomic) of normal neutral atoms. This may mean that in the apparatus used in the thermal experiments molecules are always dissociated in that way. But it need not, and probably does not, mean anything of the sort. If the molecules are first dissociated into excited atoms, and subsequently these atoms pass over into their normal state, then the energy which in so doing the atoms release is restored to the environment; and what is measured is the difference between the energy originally spent in the dissociations, and this fraction which is returned. The spectroscopic method, however, yields the amount of energy

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[3] Special methods for locating the convergence frequency must of course be employed.

which was spent in effecting that primary dissociation, with no deduction on account of the fraction thereof which may be restored by the resulting atoms in the course of their future evolution.

Now if in any particular case the state of affairs is actually such as I have just described, we may expect the "spectroscopic" value of work-of-dissociation to exceed the "thermal" value by an amount equal to the energy of excitation of one of the resulting atoms, or perhaps to the sum of two values of energy of excitation, one corresponding to each atom and the other to the other. We need not therefore be at once alarmed if we find that the spectroscopic value is greater than the thermal value. The real question will be: whether the difference may reasonably be identified with an energy of excitation or a sum of energies of excitation of the forthcoming atoms?

The outstanding example of such an identification is probably that which was established by the several contributions of Franck, Dymond, Kuhn, and Turner, of whom the first three located the band-convergence-frequencies in the spectra of iodine, chlorine, and bromine, while the last made a spectroscopic determination of the energy-difference between the normal state and the adjacent metastable excited state of each of these types of atom. (The symbols for these states are $^2P_2$ and $^2P_1$ respectively.) The agreement seems good enough to justify the supposition that when any of these molecules is split apart by absorption of radiation, one of the forthcoming atoms is in its normal state, but the other is excited. Thus for iodine, the quantum which just dissociates the molecule has an energy of 2.47 equivalent volts; the *net* work of transformation of the molecule into a pair of normal atoms is evaluated from the thermal experiments as 1.50 equivalent volts; the excess of the former over the latter agrees very well with the value 0.94 which is the energy of the excited state of the iodine atom referred to the energy of the normal state as zero. Other cases of the sort are known; particularly interesting is that of sodium iodide, in which there is independent evidence that one at least of the atoms resulting from the dissociation is excited; for the vapor when irradiated by light of frequency great enough to break the molecules apart, spontaneously emits the light (the D-lines) which is characteristic of sodium atoms passing from an excited to the normal state.

It is necessary now to take into account the fact that the stationary states of molecules must be classified (rotational fine structure being ignored, as heretofore) in a two-stage grouping: and to make this clear it is desirable to introduce the conventional molecule-model, even though in a few more years another model may supplant it.

We are, then, to visualize a diatomic molecule as a pair of massive particles—the nuclei of the two atoms—which float in a field of force so constituted that when their mutual distance d has a certain value, say d_0, they are in equilibrium. When d is greater than d_0, they are pulled together; when d is less than d_0, they are pushed apart; when d is made slightly less or greater than d_0, and the particles are thereupon left to themselves, they oscillate. The oscillations are not as a rule simple-harmonic, for the force acting on either nucleus is not as a rule strictly proportional to $(d - d_0)$. The various *vibrational states* correspond to various amplitudes of the vibration, which are determined by applying the quantum-condition when the field of force is known or postulated.

It is a sequence of such vibrational states, with vibrational quantum-numbers increasing by one unit from each to the next, which culminates in dissociation. There is however more than one such sequence. This we can foresee from the fact that the field of force is produced by the charges of the nuclei and those of the electrons jointly. Were the nuclei alone, the force would consist solely of the inverse-square repulsion which each exerts upon the other. The electrons contribute the additional force which at the distance d_0 just compensates this repulsion and at distances greater than d_0 overcomes it. Now in atoms, there are multitudes of different stationary states corresponding to different arrangements of the electrons. Molecules might be expected to resemble atoms in this respect; and as a matter of fact there are many kinds of molecules which are definitely known to exhibit several distinct arrangements of the electrons—several distinct *electronic levels,* as I will call them in order to reserve the name "state" for the various states of vibration. For, as one easily sees, to each electronic level there belongs an entire sequence of "permitted" vibration-amplitudes; and the condition of the molecule is defined when and only when both the electronic level and the vibrational quantum-number are specified. In general, the permitted values of vibration-amplitude and of vibration-energy will not be altogether the same in the sequences associated with the different electronic levels, for they are influenced by the field of force, which changes when the arrangement of the electrons is changed.

Now let us return to the case of a converging sequence of absorption bands, such as occurs in the spectrum of iodine. Here the initial state common to all the transitions of which these lines are the tokens is the vibrational state of lowest quantum-number[4] associated with the *normal* electronic level. The final states of these consecutive transitions are the vibrational states with consecutive quantum-numbers, associated with a particular *excited* electronic level. In effecting any of the intermediate steps which lead up to dissociation, and in effecting dissociation itself, the light not only increases the amplitude of the nuclear oscillations but also changes the arrangement of the circum-nuclear electrons.

How then are we to visualize the process of dissociation? According to a fertile idea first expressed by Franck, it is probably correct to regard the change in the arrangement of the electrons as the cause of the change in amplitude of oscillation, even when this is so great that the nuclei tear themselves apart altogether. When the electrons shift their places (or perhaps we should say, when the cloud of negative charge redistributes itself?) the nuclei suddenly find themselves moving with their former speeds in an entirely new field of force. Usually, though not by any means always, the equilibrium-distance d_0' in the new field is greater than the equilibrium-distance d_0 in the old. If then the nuclei are originally vibrating slightly or not at all in the

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[4] Sequences associated with vibrational states of higher quantum-numbers may also be observed.

vicinity of their former positions of equilibrium, they find themselves suddenly in a field which impels them outward; and perhaps before reaching their new positions of equilibrium they acquire so great a speed, as to dash right through these and completely out of the atom. This is dissociation. Or perhaps the speed which they acquire is not so great but that they are curbed and drawn back before they escape. In this case they continue to oscillate with an amplitude different from that which they possessed before; and this is excitation, disclosed by a line in the absorption-spectrum.

Why then, one may ask, does not always one of these things happen or always the other? Why does the rearrangement of the electrons sometimes result in dissociation and sometimes not? Probably the answer is, that even in the vibrational state of lowest quantum number, as well as the others, the nuclei are oscillating about their positions of equilibrium, so that the various molecules of a gas are at any given moment in all possible phases of vibration, and those in which the nuclei are closest together are dissociated because these particles are forced apart with great vehemence, while those in which the nuclei are farthest apart may hold together because for them the distance between the nuclei at the critical instant happens to be nearly the same as the new equilibrium-distance. It follows then that the fields of force before and after the rearrangement, and the amplitude of the vibrations before, jointly control the possibility or the relative probability of dissociation and mere change of amplitude of oscillation. Some spectra in fact reveal that both occur; in some, on the other hand, one sees only the continuous range of absorption but not a sequence of lines leading up to it; in yet others a sequence of lines fades out without reaching an obvious limit or the boundary of a zone of absorption. By means of the principle of correspondence, it is possible to draw inferences concerning the fields of force in the molecules which show spectra of any of these types.[5]

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[5] Such inferences are drawn likewise from observations on the relative intensities of the bands constituting a band-system in absorption or emission, under conditions where dissociation does not occur.

We have now considered cases in which dissociation results from the elevation, so to speak, of a molecule from its normal into an excited electronic level, this elevation being attended by so great an increase in vibrational energy of the nuclei that they tear themselves apart. There is yet another, and a very interesting, type of dissociation in which the atoms of a molecule tear themselves apart when the molecule spontaneously passes from an excited to the normal electronic level. This of course can occur only when the energy-difference between the excited and the normal level exceeds the work of dissociation—not an unusual condition among molecules, some of which can contain three or four times as much energy of excitation as would suffice, if properly administered, to disrupt them. An excellent example is furnished by the simplest of all molecules, that of hydrogen. Here we find a numerical agreement which goes far to confirm the general rightness of these interpretations of band-spectra.

In the absorption-spectrum of hydrogen there is a continuous region of strong absorption, the long-wave limit of which was located by Dieke and Hopfield at 850 Å, corresponding to 14.53 equivalent volts. Beyond this limit lie sequences of bands—not one sequence, but two—corresponding to transitions from the normal arrangement of electrons into two distinct excited arrangements. Thus light of one frequency acting upon a normal molecule may set it into augmented vibration by changing the electron-system in one way, while light of another—perhaps even of quite the same—frequency may rearrange the electrons in quite another way and likewise alter the vibration of the nuclei. Either of these transformations of the electron system may be the prelude to dissociation, and dissociation when effected consumes in either case 14.53 equivalent volts of energy; this practically proves that the resulting fragments are in both cases the same.

Now this amount, 14.53, is much in excess of the energy-difference between a pair of free normal atoms of hydrogen and a normal hydrogen molecule. This is the fact which was earlier interpreted as meaning that one at least of the atoms resulting from the dissociation is excited. At this point, however, the important feature is that the various excited states of the hydrogen molecule which are steps toward dissociation are themselves endowed with energy-values approaching 14.53, and much in excess of the energy sufficient to dissociate the molecule into two normal atoms. Does any intramolecular process ever occur whereby this amply sufficient amount of energy is actually applied to this purpose? If so, we may expect to find in the spectrum evidence of the following character:

Let us take as zero the energy of the hydrogen molecule in its normal electronic level and in its state of least possible vibration; and denote by B_n the energy of the molecule when in a certain excited electronic level (the one commonly designated as B) and in the state of n vibrational quanta. If then the molecule passes from the latter state to the former, the energy which it discharges is by definition equal to B_n. If instead it passes over not to the first but to the second vibrational state of the normal electronic level, the energy which it discharges is less than B_n; if we denote by x_2 the energy of the second vibrational state of the normal level relatively to the first, then the energy in question is $(B_n - x_2)$. Similarly if we represent by x_3, x_4, x_5 . . . . the energy-values of the third, fourth, fifth . . . . vibrational states of the normal level we shall have the sequence of energy-values $(B_n - x_3)$, $(B_n - x_4)$ $(B_n - x_5)$, and so on; and if finally this sequence of vibrational states converges at the energy-value x_∞ upon the state of dissociation, we shall have $(B_n - x_\infty)$ for the energy discharged by the excited molecule when it is dissociated upon attempting to return to the normal level. In the emission-spectrum, then, we shall find a sequence of emission-bands drawing closer together as the procession is followed from shorter wave-lengths to longer (the opposite sense from that prevailing in the sequences of which I have been writing); beyond these, a zone of continuous emission, the short-wave-limit of which, as the long-wave-limit of the sequence, yields the energy-value of the initial excited level *minus* the work of dissociation of the molecule. Now the energy-value of the initial level is itself given by the first band of the sequence. We have therefore only to subtract the limit-frequency from the frequency of the first band of the sequence, in order to obtain the work of dissociation. Witmer made the requisite observations and computations for hydrogen, and obtained for the work of dissociation the value 4.34 equivalent volts.

Here we have an apparent disagreement between two values of work of dissociation obtained both by spectrum analysis; but the meaning is the same as that of the apparent discords between the spectroscopic and the thermal measurements on iodine and other vapors. *Dissociation of the hydrogen molecule leads in the two cases to two different conditions of the resulting atoms*—a statement which is established by the same sort of numerical agreement which I quoted in the case of iodine, only here a more accurate one, since both the values which are to be compared are derived from spectroscopic measurements. The question is, whether the difference between these two values can be identified with an energy of excitation of the hydrogen atom. Now the difference between the two values is 14.53 − 4.34 = **10.19.** The least excitation-energy of hydrogen is **10.15**; and there is no other smaller than twelve volts, so that the coincidence can hardly be regarded as accidental. The almost inevitable inference is, that dissociation as the limit of the vibrational states of the normal level results in the formation of two normal neutral atoms, while dissociation as the limit of the vibrational states of the excited level *B* results in the formation of one normal and one excited atom. The "spectroscopic" value thus obtained for the heat of dissociation of the hydrogen molecule into normal hydrogen atoms far surpasses in accuracy that obtained by any other method.

The limitations of this article forbid more than a passing reference to the curious circumstance, which made the emission spectrum easy to interpret. In general, one would expect that hydrogen gas, when so violently stimulated as to emit light, would contain molecules in every vibrational state of the excited level,—a condition which would produce as many sequences of bands as there are of such states, and entail an extremely complicated spectrum. In this instance however the hydrogen was mixed with argon; and the excited atoms of argon possess just the amount of energy which, when communicated in collisions of the second kind to normal hydrogen molecules, transfers them into one particular vibrational state of the excited level.

The most interesting question remaining is probably that of the laws, if any there be, which govern the nature of the particles into which a molecule is likely to fall apart. Could we, from the chemical or physical properties of a molecular gas, predict whether on being irradiated it would resolve itself into normal neutral atoms, into excited neutral atoms, or possibly even into ions?

The facts are rather surprising. There are certain molecules, of which the alkali halides and hydrogen chloride might be taken as examples, in which it seems likely on various grounds that an electron of one atom has been taken over into the system of the other. According to the well-known octet theory the sodium atom in the sodium chloride molecule, for instance, is practically ionized, having ceded its valence electron to the chlorine atom which thus becomes practically a negative ion. There are other molecules, however, for which there is no evident reason for expecting anything of the sort; as for instance those made of identical atoms, which might be expected to have perfect symmetry.

It might then be anticipated that molecules of the former type would split by preference into ions, or at any rate into highly excited atoms; while those of the latter sort would fall apart into pairs of normal neutral atoms. Well! the surprising thing is, that so far as any rule at all emerges from the data, it seems to be the contrary of this. Molecules composed of like atoms are dissociated by absorption of light (we are not speaking of what happens when an excited molecule starts back to its normal level) into one normal and one excited atom; so also are molecules such as carbon monoxide and nitric oxide. Like them we have such supposedly outstanding examples of the other type as sodium iodide and silver iodide. On the other hand, the alkali halides display continuous zones of absorption so located as to suggest that in addition to that commoner mode of dissociation, they may separate themselves on absorbing light into normal neutral atoms. This apparent discrepancy between the facts and the expectations may however be removed by the remodeling of our expectations which the new forms of mechanics seem likely to bring about.