JULY 1, 1932 PHYSICAL REVIEW VOLUME 41

Evidence of Space Quantization of Atoms upon Impact

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(Received May 16, 1932)

The present paper offers an interpretation of certain diffuse bands observed in the spectra of metal vapors mixed with rare gases. Two separate maxima on the short wave-length side of the resonance line of the metal are not due to vibrational quanta as in the case of other similar diffuse spectra. Instead they are interpreted as separate electronic levels of the pair of colliding atoms described by space quantization taking place in the mutual approach. The diffuse structure on the long wave-length side is due to vibrational quanta of molecules.

I. Experimental Facts

SEVERAL years ago, some fluorescence experiments were performed,[1] the aim of which was to investigate the interaction in a single elementary process of the three kinds of energy: light, excitation energy, and kinetic energy of atoms. It was expected that an excited atom, when colliding with a rare gas atom, might react in two ways: either it might *split up* its energy of excitation into two parts, radiation and kinetic energy of the two atoms, thus giving rise to a continuous spectrum spreading from the resonance line to the long wave-length side; or instead the kinetic energy of impact might *join* with the excitation energy thus producing radiation that belongs to a continuum on the short wave-length side of the resonance line.[2]

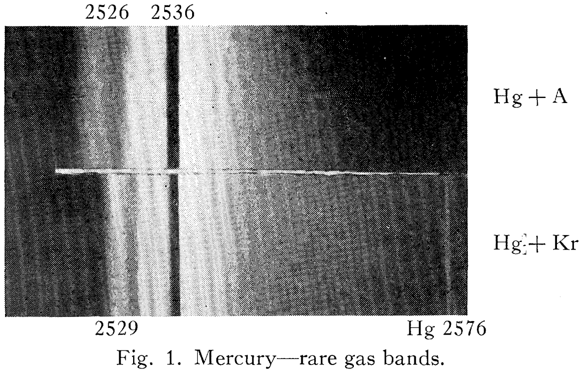

Fig. 1. Mercury—rare gas bands.

In order to check this type of interaction by experiment, the fluorescence radiation of mercury vapor with a large amount of a rare gas added has been investigated. In this experiment, the excited mercury atom has a good chance

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[1] O. Oldenberg, Zeits. f. Physik **47**, 184 (1928); **51**, 605 (1928); **55**, 1 (1929).

[2] A theoretical discussion of this process has recently been given by V. Weisskopf, Zeits. f. Physik **75**, 287 (1932) and H. Margenau, Phys. Rev. **40**, 387 (1932).

to collide during its lifetime with a rare gas atom. Actually, continuous spectra have been observed on both sides of the resonance line of mercury. Under most conditions, however, instead of having a uniform distribution of intensity, they showed an unexpected diffuse structure as seen in Fig. 1. (The intense Hg line 2537 itself was taken out of the spectrum by an absorption tube with Hg vapor, in order to prevent scattering of light at the photographic plate.) When A or Kr is added to Hg vapor, two broad diffuse maxima appear at the short wave-length side of the resonance line and a finer diffuse structure on the long wave-length side. Only a trace of structure has been observed in Hg+Ne and no structure in Hg+He or Hg+Xe.

The same type of structure has recently been observed by Krefft and Rompe[3] in mixtures of thallium and other metalic vapors with rare gases. It is of interest that also with He added they obtained two well-defined separate maxima, even broader than with the other rare gases.

II. Criticism of the Interpretation as a Band Spectrum

The fine structure on the long wave-length side has been explained by the formation of molecules from mercury and rare gas atoms. In the fluorescence experiments only the mercury, not the rare gases, was excited. It must be assumed that the excited mercury atom attracts the rare gas atom by the polarization force (cf. section IV). The conspicuous broad maxima on the short wave-length side, however, which present quite a different aspect, have not been explained satisfactorily as yet. In order to interpret them in the usual way as vibrational quanta of a band, potential curves must be assumed as in Fig. 2. The short wave-length position of the maxima must be represented by a longer vertical distance AC than FG representing the line emission. It must be assumed that excited molecules with strong vibration combine with normal molecules with no vibration or with just one quantum. It is not evident, however, why the vibration of the *excited* molecules is restricted to such a small range of high energy near A that the vibrational structure of the *normal* state comes out clearly.

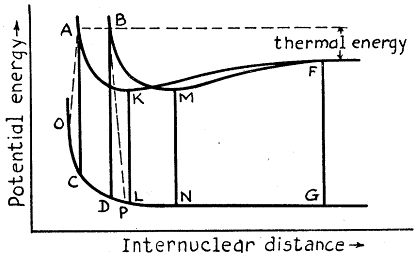

Fig. 2. Hypothetical band structure. AC, molecular band; FG, atomic line.

It has been suggested[4] that the diagram of Fig. 2 does not apply because it fails to represent the *rotational* energy of the molecule, which can exceed

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[3] H. Krefft and R. Rompe, Zeits. f. Physik **73**, 681 (1932).

[4] Oldenberg, Zeits. f. Physik **55**, 10 (1929).

considerably the dissociation energy. This argument cannot be maintained because of the selection rule. In the emission process the angular momentum of the molecule changes only by the fundamental unit $h/2\pi$. For heavy molecules as HgA or HgKr this corresponds to such a small change of rotational energy that the single band cannot spread far from its zero line. Hence the rotational energy will not affect the position of the bands to any considerable extent.

These criticisms based on a rather vague argument are strongly supported by the new observations of Krefft and Rompe, who observed the same type of structure with a particularly broad extension in the mixture of Tl vapor and He. The frequency difference between the two maxima is about 500 cm^{-1}, that is of the order of magnitude of the vibrational quantum of a regular molecule.[5] Now it cannot be assumed that the molecule TlHe exists with a considerable energy of dissociation (to be observed as a large quantum of vibration) and that it plays a part in the discharge in 800°C, for the He atom has by far the smallest polarizability[6] of all rare gases (by far the lowest condensation point, the smallest heat of vaporization, the least adsorption). Therefore the type of structure as observed in Tl+He on the short wave-length side of the Tl line must be interpreted by an entirely different process.

III. Radiation during Collision; Space Quantization

It seems that this process can be understood on the basis of the theory of band spectra without an arbitrary hypothesis. It must be assumed that the excess energy of the short wave-length diffuse structure, not explained as dissociation energy of molecules, is due to the kinetic energy of thermal impacts.[7] The mercury atom emits this radiation instead of the sharp resonance line at the moment of a collision with a rare gas atom. This is just the process mentioned above, for the study of which the experimental work was undertaken. This process has been described on the basis of potential curves by Winans and Jablonski.[8] By the same mechanism Weizel[9] recently explained the asymmetric short wave-length broadening of some helium lines discovered by Hopfield.[10] Weizel has succeeded in connecting this broadening with the

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[5] The correction discussed by H. Kuhn (Zeits. f. Physik **63,** 458 (1930) and **72,** 462 (1931)) cannot change the order of magnitude of the observed difference, while still discrete maxima of intensity are observed.

[6] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37,** 682 (1931); H. Margenau, Phys. Rev. **37,** 1425 (1931).

[7] From this assumption it follows that Condon's wave-mechanical interpretation of diffuse maxima (Phys. Rev. **32,** 866 (1928)) does not apply to the spectrum under discussion. Condon considered a sharply defined initial state (lowest vibrational level of the upper electronic state) and a final state which belongs to a continuous range. He concluded that diffuse maxima might appear closely connected with the waves representing the motion in the final state. This theory does not apply to the conditions described by Fig. 2, because here the initial state, too, is not sharply defined but is itself diffuse due to the velocity distribution. Moreover the obseved maxima seem to be broader than those described by Condon's theory.

[8] T. G. Winans, Phil. Mag. **7,** 558 (1929). A. Jablonski, Zeits. f. Physik **70,** 723 (1931).

[9] W. Weizel, Phys. Rev. **38,** 642 (1931).

[10] J. J. Hopfield, Astrophys. J. **72,** 133 (1930).

molecular spectrum. Discussing the broadening of the He line 585 on the basis of the theory of band spectra, he finds one potential curve that describes the interaction of two normal He atoms colliding with each other, and four separate curves for an excited 2^1P atom colliding with a normal one. Due to a selection rule only two of these four curves, both representing repulsion, combine with the normal state (Fig. 3).

It can be assumed that in the normal state the Hg atom has a smaller effective cross section than in the excited state. Hence in the diagram the potential curve of the normal state remains flat even for a small internuclear distance. Thus the kinetic energy of the collision—at the very moment in which it is turned into potential energy (*A* in Fig. 3)—takes part in radiating a larger quantum *AC* than the excited atom would radiate by itself (*FG*). The superimposed effect of the two potential curves of the upper state is observed as pressure broadening of the atomic line.

In the present problem—mercury with an added rare gas—the interaction of the two atoms is simpler because they are different from one another. In the normal state of the two atoms again only one potential curve exists (representing an $^1\Sigma$ term), because both the mercury and the rare gas atom have spherical symmetry in their normal ^1S states. In the upper state (excited atom+normal rare gas atom) the method of counting the molecular electronic levels, given by Hund,[11] depends upon the coupling. In Weizel's problem (He′+He) the multiplet structure (due to the interaction between the orbital momentum and the spin) is narrow as compared with the extension of the continuous spectrum (due to the interaction between the colliding atoms); this interaction between the atoms is described as a quantized orientation of the *orbital momentum* with regard to the internuclear axis. In the present problem, however, it must be taken into account that the splitting up of the multiplet structure in the mercury or thallium atom is much larger than the extension of the diffuse molecular spectrum under consideration. Hence the interaction between the orbital momentum and the spin is large

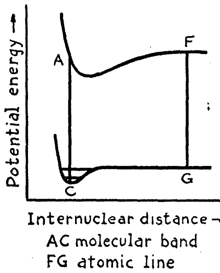

Fig. 3

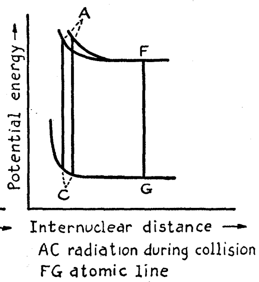

Fig. 4

Fig. 3. Radiation during collision. *AC*, radiation during collision; *FG*, atomic line.

Fig. 4. Potential curves for the mercury and rare gas collision. *AC*, *BD*, diffuse maxima on the short wave-length side; *AQ*, *BP*, limits of the spectrum; *KL*, *MN* band structure on the long wave-length side; *FG*, atomic line.

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[11] F. Hund, Zeits. f. Physik **36**, 659 (1926).

as compared with the interaction between the two colliding atoms and a quantized orientation of the *total angular momentum* of the Hg or Tl atom is to be expected with regard to the internuclear axis, just as in the case of a Stark effect in a weak electric field. The number of separate energy levels of the Hg′ or Tl′ colliding with a normal rare gas atom is given by the number of terms in the series $j, j-1 \cdots, 0$ or $\frac{1}{2}$. (Negative values of j describe another orientation but give the same energy levels as the positive values of j).[12] This argument leads to the conclusion that in the upper state $\mathrm{Hg}'(2^3P_1)+$rare gas (^1S) two molecular levels exist, given by $j=1$ and $j=0$, represented in the diagram by two separate potential curves. From both excited levels the transitions to the normal level are allowed. (As in general the collision will not be head on, a rotation will be superimposed with a constant angular momentum.)

Along one or the other of these curves the rare gas atoms and the mercury atoms will approach each other to a certain range of potential energy A or B determined by the thermal energy.

The effective cross section of the Hg atoms in the normal state will be supposed to be smaller than in the excited state. Hence the lowest potential curve of Fig. 4 representing the normal state will just barely begin to rise for the values of nuclear distance that belong to A and B. Therefore both transitions AC and BD, that are vertical in the diagram—following the Franck-Condon rule—represent radiations of larger energy or shorter wave-length than the atomic line FG, BD shifted by a larger amount than AC. This reasoning leads to two separate diffuse maxima on the short wave-length side of the atomic line, both of them shifted by an amount smaller than the mean kinetic energy of the collisions. This just describes the observed spectra. The two separate maxima are interpreted not by the vibration of a molecule but by two separate electronic levels of a pair of atoms to be described by two separate directions of mutual approach, both of them belonging to the same electronic levels of the atoms. Thus the separate maxima give evidence of space quantization in the collision between atoms. This interpretation is strongly supported by the fact that the two separate maxima persist at high temperature (cf. section IV).

The diffuse bands show a rather sharp limit on the short wave-length side and in some cases a much longer diffuse extension to long wave-lengths. This may be understood, too, on the basis of the potential curve diagram (Fig. 4). The dotted lines represent transitions in the case of a small change of internuclear distance during radiation. The long distance BP, representing radiation of short wave-length, cannot be much longer than BD, representing the most probable transition from B. AQ, however, representing the long wave-length extension, can be considerably shorter than AC due to the steep branch of the lower potential curve.[13]

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[12] Cf. W. Pauli, Handbuch d. Physik XXIII, p. 246.

[13] The extension to long waves plays the major part in the absorption experiments. at high pressures of Füchtbauer, Joos and Dinckelacker (Ann. d. Physik **71**, 204, (1923)) and Bonhoeffer's and Reichardt's experiments with Hg dissolved in liquids (Zeits. f. Physik **67**, 780 (1931)).

The appearance of the same diffuse structure in the *absorption* spectrum will be explained by the inverse process, the absorption being produced by a mercury atom at the moment of a collision with a rare gas atom.

That these *separate* maxima were not observed by Hopfield in the spectrum of helium, was probably due to their position in the extreme ultraviolet, where the resolution of the same differences in frequency is much more difficult.

The diffuse maxima, reported by Krefft and Rompe in thallium vapor with an added rare gas near the green thallium line $2^2S_{1/2}-2^2P_{3/2}$, are explained by separate molecular levels ($j=\pm 3/2$ and $\pm 1/2$) belonging to the *lower* atomic level instead of the upper one. All other observations, too, can be interpreted on the same basis. One cannot expect, however, to observe separate maxima in every case, for which they are derived from the theory, because they may overlap too much. This is evidently the case in Hg+He, where the existence of two maxima can only be deduced by analogy with the other rare gases.

IV. QUANTIZED MOLECULES FORMED OF EXCITED MERCURY AND RARE GAS ATOMS

This explanation does not take into account the finer diffuse structure on the long wave-length side of the atomic line (Fig. 1). Its previous interpretation as oscillation quanta of a molecule will be maintained.[14] The simple structure and its position on the long wave-length side is most easily explained—contrary to the explanation published previously—by the formation of molecules of Hg atoms in their *excited* state with rare gas atoms. One expects the excited Hg atom to be able to induce an electric moment in the rare gas atom and thus by polarization form a loosely bound molecule. The normal Hg will have this power to a smaller extent because it has a high symmetry similar to that of a rare gas atom. Therefore the upper potential curves of Fig. 4 ought to show shallow minima for large values of the internuclear distance, for which the lower curve is approximately flat. This type of excited molecule would emit a diffuse band on the long wave-length side of the atomic line, in which the vibrational quanta still might be distinguished.

Hence this band system is explained by a group of vibrational levels in the *upper* electronic state combining with a lower state in which vibrational levels can not be resolved. It has been described as an apparently simple set of bands with a trace of convergence to the long wave-length side; it has been mentioned, however, that possibly the observed set of bands is due to the superposition of several sets. According to the present interpretation, two simple sets of bands (*KL* and *MN*, Fig. 4) belonging to the two upper potential curves should be superimposed. The smaller slope of the potential curve of the normal state might modify the position of the observed bands. Therefore no conclusion can be drawn concerning the convergence from the structure as shown in Fig. 1.

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[14] Cf. F. London, Zeits. f. Physik **11**, 248 (1931).

This interpretation of the diffuse structure on the long wave-length side as vibrational quanta of a band system is supported by observations. This structure does not appear for the light atoms He and Ne, which—due to their smaller polarizability—might not form molecules. (It remains uncertain if this type of structure exists for Hg+X. The pictures with Xenon were taken with a quartz bulb of a few millimeter diameter, from which the scattered light was so strong that the structure might have been concealed.) At high temperature the fine structure on the long wave-length side disappears, while the broad maxima on the short wave-length side remain (observed in Hg+A). This is understood as the complete dissociation by heat; in these circumstances there will remain only the broad maxima on the short wave-length side that are explained not by vibrations of molecules but by separate electronic levels of a pair of colliding atoms.

V. Conclusion

We come to the conclusion that three different processes are to be distinguished in the collision of Hg′ with a rare gas atom. In most cases the atoms will separate without any effect, leaving the Hg′ such that it radiates its sharp atomic line (*FG* in Fig. 4). This may be the most probable process. In some other cases the radiation will take place in the moment of the collision giving rise to the broad maxima on the short wave-length side of the atomic line (*AC* and *BD* in Fig. 4). Finally in a few cases, if the temperature is not too high, some energy may be taken away in a triple collision;[15] real excited molecules with vibrational quanta will be produced emitting a band spectrum (*KL* and *MN* in Fig. 4).

The diffuse maxima in the fluorescence radiation of mercury vapor with a rare gas added are surprisingly intense. The corresponding spectra in the neighborhood of some other lines, for instance the *D* lines of Na, are much fainter or missing entirely. This leads to the question, whether in some atomic terms, but not in all of them, the collision process might produce an instantaneous increase in the probability of emission. This problem will be further investigated.

According to the present interpretation, the main conclusion is that the two separate maxima of intensity, observed in the spectra of certain metal vapors mixed with rare gases, furnish evidence that the mutual approach of these atoms can be described by space quantization.

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[15] M. Born and J. Franck, Ann. d. Physik **76**, 225 (1925).

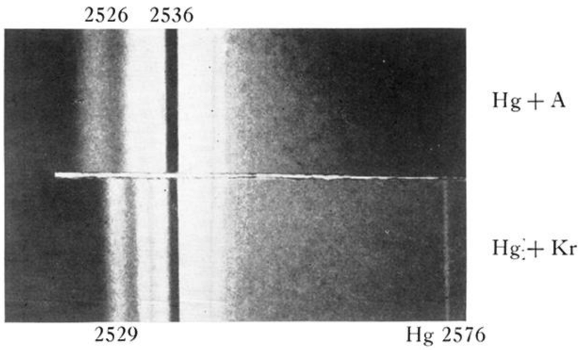

Fig. 1. Mercury—rare gas bands.