

X-RAY OUTPUT

The generator can be operated at all voltages from 200 kv to 1250 kv with a current on the target of well over one milliamper. At 1250 kv with about 5 mm of lead equivalent filtration, the x-ray intensity per milliamper in the downward direction 50 centimeters from the target is about 340 roentgens per minute. Various measurements of the physical properties of the radiation produced are now being made.

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Dipole-Dipole Resonance Forces

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London has shown that at fairly large interatomic distances r , the polarization energy of a molecule composed of two identical atoms varies not as the customary r^{-6} , but rather as r^{-3} in case one atom is in the ground state, and the other is in an excited state which can combine by dipole transitions with the ground level. The present paper is concerned with the size and sign of this dipole-dipole resonance energy obeying the inverse cube law. The sign has no immediate relation to the sign of the exchange and penetration forces which predominate at closer approach. This possibility of a change from repulsion to attraction results in one of the stable levels of the group of first

excited states (derived from separate atom configuration $S+P$ for example) having a lip of activation energy before decomposition into atoms. There will also be a "repulsive" state having a shallow minimum at large separations. Molecules of the heavy atoms have an activation lip so large that the whole stable region is above the dissociation energy. Potential curves of this type have previously been derived empirically from spectroscopic analysis in the case of Hg_2 and Cd_2 . The lip is less pronounced in lighter atoms but is none the less real, and has experimental confirmation in the Na_2 spectrum.

INTRODUCTION

IT IS well known that the polarization of van der Waals energy of a molecule composed of two unexcited atoms varies as the inverse sixth power of the interatomic distance r . The inverse third power, however, occurs for a molecule composed of two identical atoms when one of them is in the ground state, and the other is in an excited state which can "combine," in the spectroscopic sense, with the normal state. The mathematical origin of this anomalous inverse cube energy is quite clear. In the energy matrix the elements connecting the different approximate states are, at large distances, dipole-dipole

interactions proportional to $1/r^3$. In the diagonalization of the matrix by perturbation theory such nondiagonal terms in general occur as the square, $\sim 1/r^6$, in the energy expression, corresponding to the potential of the familiar van der Waals forces. If, however, there is degeneracy, the nondiagonal elements appear to the first power, $\sim 1/r^3$ in the energy expression. Physically this kind of coupling could be described as exchange of excitation—the de-excitation of one atom with excitation of the other. The existence of a $1/r^3$ term was first pointed out by Eisenschitz and London¹ in the first excited states of H_2 . Such a term, however, will occur in certain

* This work was done as a National Research Fellow, 1937.

¹ R. Eisenschitz and F. London, *Zeits. f. Physik* **60**, 491 (1930). See also H. Margenau and W. W. Watson, *Rev. Mod. Phys.* **8**, 33 (1936).

levels of any molecule formed of like atoms, and often is of considerable magnitude and long range. It is the purpose of the present paper to examine it somewhat more thoroughly than previously.

CALCULATION OF THE INTERACTION

The only molecular states in which such forces occur are those composed of atoms in states between which there is a dipole moment, e.g., $S+P$, $P+D$, etc. The most important cases are the states arising from the configuration $S+P$.

At distances where electronic exchange integrals are small, molecular binding is Hund's case b ; single electronic eigenfunctions need be used no longer, but simply functions of the atom as a whole, say S and P . That is, the approximate molecular functions may be taken as SP and PS , the notation PS indicating interchange of the whole atoms. We must make a definite convention once and for all about this operation of "interchange of atoms," say

$$x_i, y_i, z_i \text{ (atom 1)} \rightarrow x_i, y_i, z_i \text{ (atom 2)}, \quad (1)$$

where the x, y, z , coordinates of each atom are parallel. In what follows, we shall take the z axes to be parallel to the internuclear axis. This definition of "interchange" means simple translation, with no reflection in center of gravity. The latter definition, of course, would be just as good.

The mathematics of finding the energy levels and the wave functions is the same as in the Heitler-London treatment of the hydrogen molecule. The energy matrix (Slater's notation) is, allowing for nonorthogonality

$$\begin{pmatrix} (SP, H SP) & (SP, H PS) \\ (PS, H SP) & (PS, H PS) \end{pmatrix} \times \begin{pmatrix} 1 & (SP, PS) \\ (PS, SP) & 1 \end{pmatrix}^{-1} \quad (2)$$

with energy levels

$$W = \frac{[(SP, H SP) \pm (SP, H PS)]}{[1 \pm (SP, PS)^2]} \quad (3)$$

for eigenfunctions symmetric S^A and antisymmetric A^A with respect to interchange of the

atoms. The corresponding wave functions are

$$\psi = (SP \pm PS) / [2 \pm 2(SP, PS)^2]^{\frac{1}{2}} \quad (4)$$

We shall henceforth disregard the small non-orthogonality corrections and so treat the denominator of (3) as unity.

Perturbation energy

In the general case of n electrons in each atom the perturbing part of the Hamiltonian is

$$H' = \sum_{i,j} \left[-\frac{eE_A}{r_{iB A}} - \frac{eE_B}{r_{iA B}} + \frac{e^2}{r_{ij}} + \frac{E_A E_B}{r} \right], \quad (5)$$

that is, the potential of the electrons of one atom in the field of the other nucleus, and the mutual repulsions of all the electrons and of the two nuclei.

Whatever the value of n this potential function may be expanded in a Taylor series to give, in terms of the Cartesian coordinates of the electrons,

$$\begin{aligned} r^3 e^{-2} H' = & \left(\sum_i^n x_{iA} \right) \left(\sum_i^n x_{iB} \right) + \left(\sum_i^n y_{iA} \right) \left(\sum_i^n y_{iB} \right) \\ & - 2 \left(\sum_i^n z_{iA} \right) \left(\sum_i^n z_{iB} \right) \quad (6) \end{aligned}$$

plus higher terms. The terms written are dipole-dipole interactions.

Thus the matrix element $(SP, H' SP)$ is zero, while the atom exchange element $(SP, H' PS)$ becomes

$$\begin{aligned} e^2 r^{-3} \left[\left(\int S \sum x_i P dT \right)^2 + \left(\int S \sum y_i P dT \right)^2 \right. \\ \left. - 2 \left(\int S \sum z_i P dT \right)^2 \right]. \quad (7) \end{aligned}$$

Now in the spherical symmetry of the atomic field the dipole moment induced in any *one* of the Zeeman components of the atomic transition $S \leftrightarrow P$ is (x, y, z , being equivalent)

$$\mu_m = e \int S \sum q_i P d\tau \quad (q = x, y, z). \quad (8)$$

Thus the difficult part of the molecular calculation is referred back to the theory of atomic

structure. The dipole moment μ_m may be obtained either from theory (as in the case of H or Na) or from experimentally determined values of the number of dispersion electrons,

$$\mu_m^2 = f_{ij} R / \nu_{ij} g_j, \quad (9)$$

where g_j is the weight factor of the lower state, and ν_{ij}/R is the energy of the transition in atomic units (R being the Rydberg constant). Note that the square of the dipole moment associated with a normal atomic transition is three times this expression (9), as one sums over the three Zeeman components, i.e., over m . There are then no undetermined constants in our calculations, as μ_m can thus be regarded as known.

The energy of interaction is then proportional to μ_m^2/r^3 , the proportionality factor depending on the orientation of the P state to the molecular axis. In the language of resonance phenomena, as an S and a P atom approach, each atom resonates between its S and its P state. The coupling energy is due to the interaction of the two dipoles induced by this resonance, or *atom-exchange*, the magnitude and sign depending on the orientation of the dipoles with respect to the internuclear axis.

Our molecular states $SP \pm PS$ have a threefold orbital degeneracy at infinite internuclear distance because of the three possible orientations of the orbital angular momentum. At closer approach, however, the energy is different for the Σ and Π levels, which have, respectively, $\Lambda = 0$ and $\Lambda^2 = 1$, where Λ is the component of orbital angular momentum parallel to the figure axis, measured in multiples of $\hbar/2\pi$. The Π levels are, of course, doubly degenerate because of the two sign possibilities for Λ . Now the matrix elements of z vanish unless $\Delta\Lambda = 0$, while those of x, y obey the selection rule $\Delta\Lambda = \pm 1$. Hence for Σ states, the expression (7) becomes $-2\mu_m^2/r^3$, because the integrals (8) over x and y are zero. For Π states,

on the other hand, (7) gives μ_m^2/r^3 since here the integral² over z and over x or y disappears.

It is customary to classify molecular states as g or u according as they are even or odd under reflection in the center of symmetry, midway between the nuclei, defined by the operation

$$x_i, y_i, z_i \text{ (atom 1)} \rightarrow -x_i, -y_i, -z_i \text{ (atom 2)}. \quad (10)$$

Now the reflection (10) can be interpreted as a translation (1) followed by a reflection in a nucleus. Furthermore the atomic wave functions S and P must have opposite symmetries or Laporte parities as regards nuclear reflection because otherwise the S and P states could not combine in dipole transitions, as we have supposed. It therefore follows that the substitution (10) takes the wave function SP into $-SP$, and that the upper and lower sign choices in (3) or (4) correspond to u and g states, respectively. Taking into account the results of the preceding paragraph, we thus find that the inverse cube term in the energy has the values given in Table I. The coefficients for the Π but not the Σ states were also previously calculated by Eisenschitz and London. Table I is applicable regardless of the multiplicity, i.e., whether the state is a singlet, triplet, etc., since the symmetry as regards electron in distinction from atom exchange has not entered into our calculations in any way. It is also to be noted that our computations are independent of the number of electrons in the system: the energetics of a diatomic molecule, at fairly large distances, has been reduced to a two-body problem, although the two bodies individually may be very complex, the only requirement for our calculations being that the transition probabilities between their states are available.

Since electron-exchange integrals die out ex-

TABLE I. *Coupling energies of the four distinct states.*

| STATE | WAVE FUNCTION | COUPLING ENERGY |
|------------|---------------|-----------------|
| Σ_u | $SP+PS$ | -2 |
| Π_u | | +1 |
| Σ_g | $SP-PS$ | +2 |
| Π_g | | -1 |

² Each Π level is twofold except insofar as the degeneracy is lifted by molecular rotation giving the phenomenon of "A-type doubling" which we neglect. We need not enter into the question of the precise linear combinations of wave functions appropriate to the two components of the Λ -doublet, and instead for our purposes the Π levels may be supposed to have a cosine or sine azimuthal factor, so that either the x or y component drops out. With exponential azimuthal functions, there are both x and y contributions, but then there is an additional factor $\frac{1}{2}$, so that in any case the absolute value of the coefficient of our $1/r^3$ term is half as large for the Π as the Σ states. That $\mu_x^2 + \mu_y^2$ gives no bigger effect than μ_z^2 is essentially a reflection of the fact that the x, y intensity must be apportioned between the two practically coincident Π states.

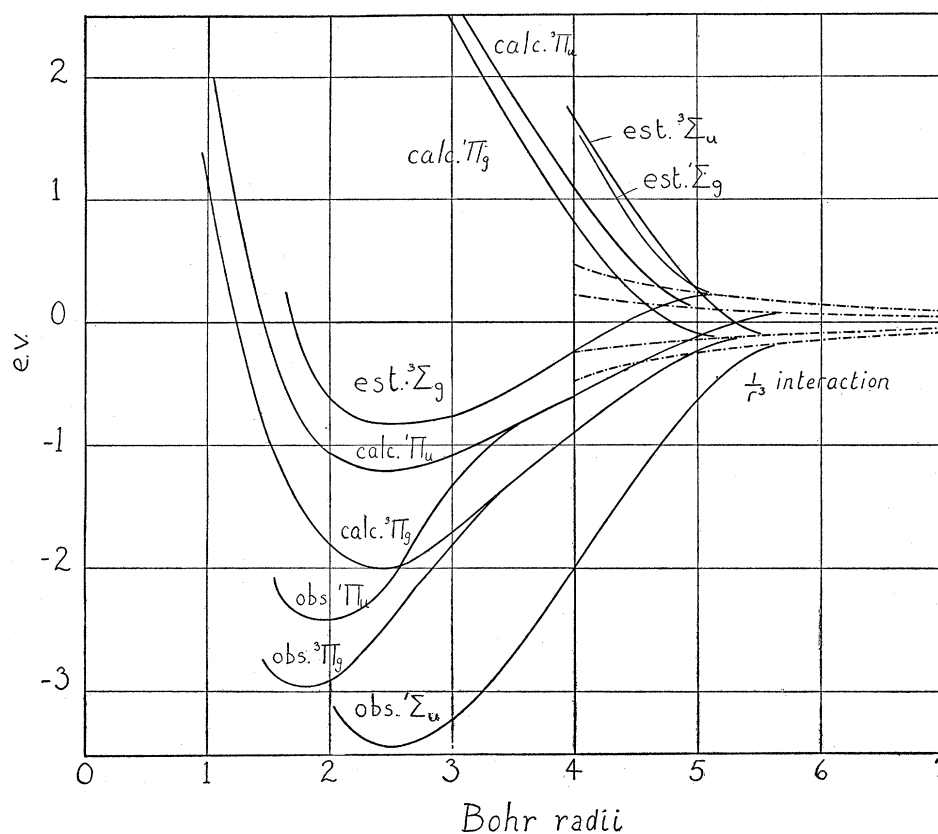


FIG. 1. First excited states of H_2 . The curves $C^1\Pi_u$, $B^1\Sigma_u$, $^3\Sigma_g$ are known experimentally in the neighborhood of their minima. The course of the Π states have been calculated theoretically as far as $4a_0$ by Kemble and Zener (reference 4). The Σ states have been sketched in by analogy, the \cdots curves at the asymptotic μ^2/r^3 curves.

ponentially the above calculations will give the correct interaction at large distances. At shorter distances, exchange becomes predominant, but the sign of the total exchange terms has no relation to the sign of the $1/r^3$ term. Some states then may be repulsive at large distances, but attractive and stable closer in, and vice versa. For atoms with one valence electron, each one of the states listed in Table I corresponds to a singlet and a triplet, and in general one of these multiplets will change the sign of its interaction as the atoms approach to distances where electron exchange predominates.

Thus it is possible to have an activation energy of dissociation, the $1/r^3$ force causing a peak or lip in the potential curve, above the limit of dissociation energy (see figures).

Similarly, the $1/r^3$ term may be attractive re-

verting to a repulsive electronic exchange term, thus giving rise to a stable molecule only at fairly large distances.

The actual magnitude of the activation lip, or the small dissociation energy just mentioned, is very sensitive to the balance of the exchange and $1/r^3$ terms at moderate distances. All molecules in the states discussed, i.e., those formed from $S+P$ atom states, will have the μ^2/r^3 energy at some separation r . In some molecules we believe this activation energy is detectable.

In other cases the effect of this term is detected only in the anharmonicity in the upper slopes of the potential curve, showing up as a change in the course of the Birge-Sponer extrapolation of the vibrational levels.³

³ W. Jevons, *Band Spectra of Diatomic Molecules* (Cambridge Univ. Press, 1932), p. 194.

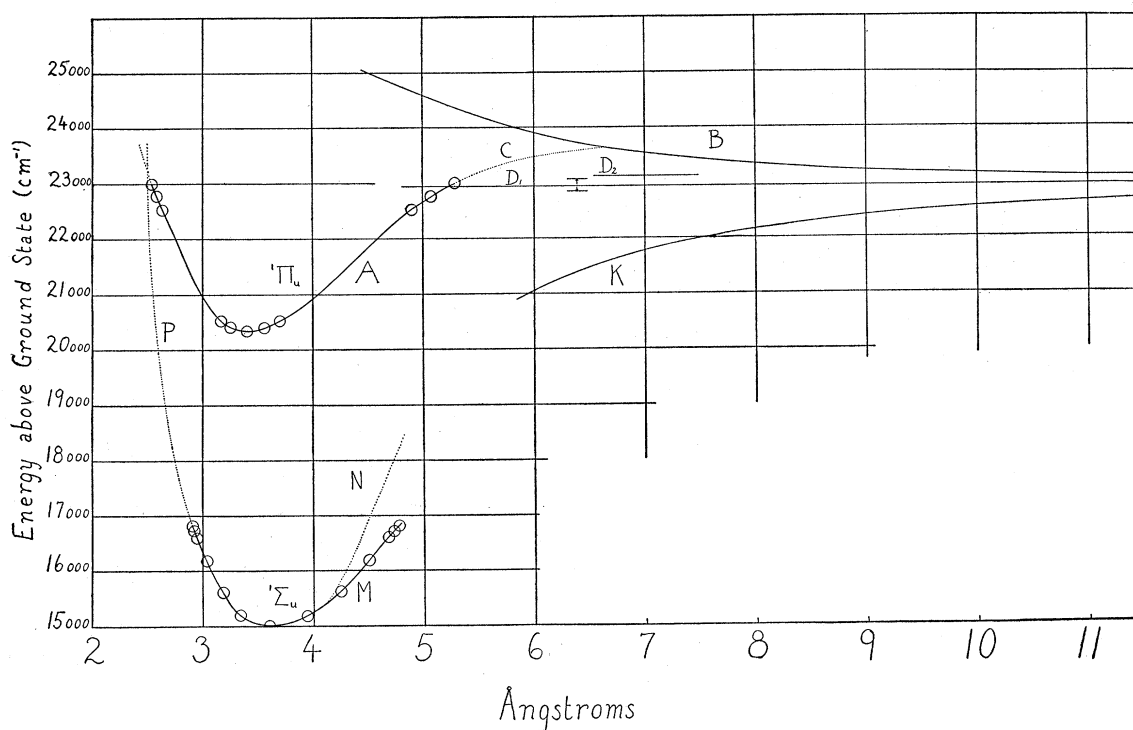


FIG. 2. First excited states of Na_2 . The circles represent points calculated from the experimental data.

APPLICATIONS

Hydrogen

The asymptotic interaction energies calculated for H_2 and Na_2 are plotted in Figs. 1 and 2. The dipole moment μ for these atoms can be obtained from theory. For the $1s-2p$ transition of hydrogen, $\mu = 0.745$ atomic unit, so the interaction energy of $\text{H}(S)$ and $\text{H}(P)$ becomes $15 \text{ ev}/r^3$, with r measured in atomic units (Bohr radii). The potential curves of all the states arising from this configuration are drawn in Fig. 1.

The effect of the $-2\mu^2/r^3$ term is definitely detected in the shallow experimentally determined curve of $B^1\Sigma_u$. The curve of $C^1\Pi_u$ has not been followed experimentally close enough to the dissociation limit to make connection with the predicted $+\mu^2/r^3$ lip, but its sharp rise and low anharmonicity relative to B indicates the course may be as in Fig. 1.

The electronic exchange energy in the Π states has been calculated by Kemble and Zener,⁴ and the courses of the $^1,^3\Sigma$ states have been sketched

⁴ E. Kemble and C. Zener, Phys. Rev. **33**, 512 (1929).

in by analogy. Both $^1\Pi_g$ and $^3\Sigma_u$ are repulsive except for shallow minima at $4a_0$ but as far as we know these stable levels have never been observed.

Since the basis functions ($1s$ and $2p$) used by Kemble and Zener, are the true atomic function in this case of hydrogen, namely our S and P , the curves calculated for the Π states should agree exactly with our dipole-dipole calculation at larger distances of separation.

Alkali molecules

The potential curves⁵ of the $^1\Sigma_u$ and $^1\Pi_u$ states of Li_2 , Na_2 and K_2 very definitely show the effect of the $1/r^3$ term, the $^1\Pi_u$ potential curve rising sharply and the $^1\Sigma_u$ curve being very shallow. The vibrational levels have been measured to very high quantum numbers permitting the construction of the potential curves almost to the dissociation limit.

In the case of Na_2 there is a possibility of an actual activation lip, i.e., there are vibrational

⁵ See, for example, H. Sponer, *Molekulspektren II* (Julius Springer, Berlin, 1935), p. 155, Fig. 53.

TABLE II. Table of f values and dipole-dipole interactions, calculated from Eq. (9).

| ATOM | $\lambda A(S \leftrightarrow P)$ | ν/R at.u. | f_{S-P} | μ_m^2 at.u. | μ_m^2/r^3 EV/A ³ |
|------|----------------------------------|----------------------|---------------------|--------------------|---------------------------------|
| H | 1215 | 0.7500 ¹⁸ | 0.416 ¹⁹ | 0.555 | 2.2 |
| Li | 6708 | 0.1358 | 0.7500 | 5.52 | 22.0 |
| Na | 5893 | 0.1546 | 0.9755 | 6.31 ²⁰ | 25.2 |
| K | 7699 | 0.1184 | ~ 0.98 | 8.28 | 33.0 |
| Rb | 7900 | 0.1154 | ~ 0.98 | 8.47 | 33.8 |
| Cs | 8943 | 0.1019 | 0.98 | 9.62 | 38.4 |
| Zn | 2139 | 0.4261 | ~ 1.2 | 2.82 | 11.2 |
| Cd | 2289 | 0.3981 | 1.20 | 3.01 | 12.0 |
| Hg | 1850 | 0.4926 | 1.19 | 2.42 | 9.6 |

¹⁸ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 133.

¹⁹ Y. Sugiura, *J. de phys. et rad.* **8**, 133 (1927).

²⁰ Y. Sugiura, *Phil. Mag.* **4** 502 (1927) calculates a value of 18.89 for $\sum_m \mu_m^2 = 3\mu_m^2$ for Na.

levels beyond the dissociation limit as determined from the chemical estimate of the dissociation energy. The Birge-Sponer extrapolation, plotting the vibrational energy against the difference in successive levels, given by Loomis and Nusbaum,⁶ has been followed experimentally to within 0.02 ev of the limit, and predicts a dissociation energy (of the ground state) of 0.76 ± 0.02 ev, the last measured point, Fig. 2, corresponding to a value of 0.74 ev. The chemical evidence of Lewis⁷ gives 0.728 ± 0.013 ev. The sharp break in the extrapolation curve,⁶ marks the onset of the $1/r^3$ law.

In Fig. 2, curve A is the potential curve of the ${}^1\Pi_u$ state of Na_2 constructed from the experimental data⁶ by O. Klein's⁸ formulation of Rydberg's method, $\oint p dr = (v + \frac{1}{2})h$, etc. That is, curve A can be considered as having been determined experimentally. The width of each level, $r_{\max} - r_{\min}$, is accurately known from the vibrational energy. The positions of the walls of the potential curve are fixed by $1/r_{\max} - 1/r_{\min}$, determined from B_v . Since the latter are not known at the higher levels except by extrapolation of $B_v - \alpha(v + \frac{1}{2})$ the curve as drawn may not be pushed sufficiently far out. However, even in the most extreme case⁹ the upper slopes of ${}^1\Pi_u$ show that it will be difficult to extrapolate to the dissociation energy calculated as $22,952 \text{ cm}^{-1}$ from the chemical determination of the ground state dissociation energy,⁷ $5900 \pm 100 \text{ cm}^{-1}$ plus atomic activation $16,966$, (represented by D_1 on the diagram).

On the contrary the curve definitely tends to the limiting $+ \mu^2/r^3$ law (curve B) plotted upwards from $22,952 \text{ cm}^{-1}$.

⁶ F. W. Loomis and R. E. Nusbaum, *Phys. Rev.* **40**, 384 (1932). The convergence limit thus calculated is marked as D_2 in Fig. 2.

⁷ C. Lewis, *Zeits. f. Physik* **69**, 786 (1931).

⁸ O. Klein, *Zeits. f. Physik* **76**, 226 (1932).

⁹ The fact that the inner wall cannot have an overhang, i.e., r_{\min} undoubtedly decreases as the energy increases, affords a limit to the possible displacement of the (known) width $r_{\max} - r_{\min}$.

The upper slopes of A can be fitted by $E = 23,840 - 3520/r^6$, which function was used to interpolate (curve C) between the "experimental" curve A and the limiting curve B .

Predissociation.—Examination of the observed intensities⁶ of the v' -progressions leads one to expect some $v' = 27$ bands to appear with considerable intensity, whereas in actual fact there is a complete cut-off after $v' = 26$, indicating some sort of predissociation.

The value of $2^3 \pi h^{-1} m^3 \int (E - V(r))^{1/2} dr$ obtained from our combination curve C, B , is 300 for $v' = 26$, and is 40 for $v' = 29$. Thus a sudden decrease occurs after $v' = 26$, but these estimates are too large for appreciable predissociation even in the latter case, as the significant exponential factor would be about e^{-80} . However, these values are for zero angular momentum; the curves for nonzero values of J lie above that of Fig. 2, and the average probability of predissociation for the whole band is somewhat greater.

The error in the construction of the curve mentioned above would favor a lower potential hill. However, it is the thickness, i.e., the $1/r^3$ effect, rather than the height that prevents predissociation.

The other possible cause of predissociation, proximity of another state into which a radiationless transition can occur, may be effective here. The only permissible perturbing state of Na_2 is the ${}^1\Sigma_u$, which conceivably might cross ${}^1\Pi_u$ at a radius less than the equilibrium value, near r_{\min} , and not having the lip, could permit predissociation. If so, the ${}^1\Sigma_u$ state would have to be sharply repulsive at small distances, as shown by the dotted line in Fig. 2. The ${}^1\Sigma_u$ and ${}^1\Pi_u$ levels can interact when rotational distortion terms in the Hamiltonian function are included.¹⁰ The possibility that at small distances the ${}^1\Sigma_u$ curve actually crosses above the ${}^1\Pi_u$ is not merely an *ad hoc* suggestion, for it is indicated by two lines of evidence, *viz.* by the higher vibration frequency for ${}^1\Sigma_u$ than for ${}^1\Pi_u$ and also by the fact that ${}^1\Pi_u$ coalesces¹¹ into a state of lower energy for the united atom than does ${}^1\Sigma_u$.

The experimental data for the ${}^1\Sigma_u$ state have not been extended to high enough v 's to make the connection with $-2\mu^2/r^3$. Curve M is constructed by the Klein-Rydberg method, curve N by Condon's formulae¹² as given by Loomis and Nile.¹³

In Li_2 too, the vibrational levels have been observed¹⁴ to within a few hundredths of a volt of the dissociation limit. The value calculated for the dissociation energy of the ground state is 1.14 ev, considerably higher than the value of 1.02 ev obtained by other means.⁷

¹⁰ R. de L. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, 1930), Chap. II.

¹¹ R. S. Mulliken, *Rev. Mod. Phys.* **4**, 1 (1932), especially Fig. 43.

¹² E. U. Condon, *Phys. Rev.* **28**, 1182-1201 (1926).

¹³ F. W. Loomis and S. W. Nile, *Phys. Rev.* **32**, 873 (1928).

¹⁴ F. W. Loomis and R. E. Nusbaum, *Phys. Rev.* **38**, 1447 (1938).

The chemical dissociation energy¹⁵ of K_2 is within the experimental error the value obtained by extrapolation of the vibrational levels. The lip must be very small in the case—the negative exchange integrals extending a little further out than in Na_2 .

In Rb_2 the value of the dissociation energy obtained by extrapolation of the levels of $^1\Pi_u$ state,¹⁶ is very high, showing the steep rise due to the positive $+\mu^2/r^3$ term.

In these alkali molecules the dipole moment produced in the atomic transition is extremely large, making the $1/r^3$ interaction unusually large and of long range, as shown in Fig. 2 and Table II. This effect will then cause considerable self-broadening in the atomic lines of the alkalis.

Cadmium

The calculation of the $1/r^3$ interaction energy is independent of the number of electrons. Consequently the same formulas (Table I) apply to the first excited states of He_2 , Hg_2 , Cd_2 , Zn_2 , even though there are now two valence electrons per atom, so that the coupling is of the type s^2-sp rather than $s-p$. There is experimental evidence on the importance of this type of interaction in the spectra of Hg_2 and Cd_2 .

Cram¹⁷ has analyzed the bands of Cd_2 lying on either side of the $^1S_0-^1P_1$ atomic line and can only account for the spectra by assuming a curve of the type drawn in Fig. 3 for the state $\Lambda=1[^1\Pi_u]$ arising from the configuration $5S+5P$.

The dipole moment of the atomic transition $S\leftrightarrow P$ of Cd can be calculated from the experimentally determined f values (see Table II). In Fig. 3, the course of the molecular energy of Cd_2 at large distances is drawn, B , from the state having the asymptotic energy $+\mu^2/r^3$. The curve A is the experimentally determined potential curve for the state $\Lambda=1$ which differs from $+\mu^2/r^3$ by the predominance of stabilizing exchange, etc. energy at closer approach. Thus the difference of A and B , represented by C , is an empirical determination of exchange and penetration energies. This curve compares favorably with that for the binding energy in normal molecular states—where the asymptotic expression is of the van

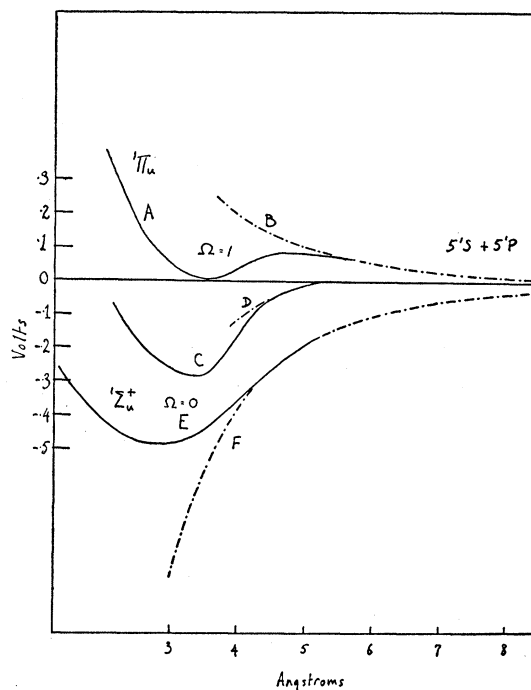


FIG. 3. First excited states of Cd_2 , bordering the atomic line $5S_0-5P_1$. Curve A was determined by Cram (reference 17). B and F are the μ^2/r^3 limiting laws.

der Waals $1/r^6$ type. Curve D is an example of the latter as obtained from the calculated $1/r^6$ curve for normal Hg_2 (see below) modified for the larger dipole of Cd. Comparison of D with B or F shows the essential difference between $1/r^3$ and $1/r^6$ forces, i.e., between resonating and induced dipole-dipole interactions.

Curve F is the $-2\mu^2/r^3$ energy of another stable state of Cd_2 , $\Lambda=0$, sketched as E .

Mercury

This same type of potential curve, with a minimum above the dissociation limit has been deduced²¹ from the spectrum analysis of Hg_2 for the state $\Lambda=1$ arising from the configuration $6S_0+6P_1$, and is likewise predicted by theory. The curves of Fig. 4 show the experimental, calculated, μ^2/r^3 exchange and van der Waals energies, as described under "Cadmium." The μ of the calculated curves of Hg (B and F) were obtained from the f values of the $^1S_0\leftrightarrow^1P_1$ transition of atom Hg (Table II). The van der Waals

¹⁵ C. Lewis, reference 7, corrected by F. W. Loomis and R. E. Nusbaum, Phys. Rev. **39**, 89 (1932).

¹⁶ P. Kusch, Phys. Rev. **49**, 218 (1936).

¹⁷ Winston Cram, Phys. Rev. **46**, 205 (1934).

²¹ W. Finkelburg, *Kontinuierliche Spektren* (Julius Springer, Berlin, 1938), p. 204.

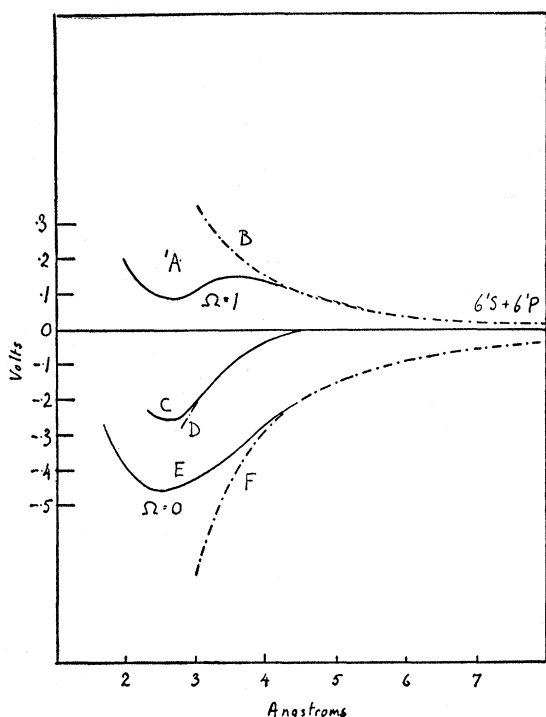


FIG. 4. First excited states of Hg_2 , bordering the atomic line $6S_0-6P_1$. The course of the level $\Lambda=0$ was predicted by spectroscopic analysis by various observers (reference 21).

expression for normal Hg_2 , curve D has been calculated as $-159 \text{ ev}/r^6$ (r in A) by F. London.²²

SUMMARY

One level of the group of first excited states of all identical molecules has an asymptotic coupling energy $+\mu^2/r^3$ above the dissociation limit. In molecules composed of atoms of low atomic number, the stabilizing energy (exchange, etc.) has fairly long range and quenches the $1/r^3$ term

to an almost insignificant lip (that is, the negative energy does not change over to $+\mu^2/r^3$ until r is very large). However, in heavy atoms, the $1/r^3$ term is powerful enough to keep the whole stable region above the dissociation limit. There levels may lose much of their sharpness due to penetration of the potential barrier.

This type of curve should be found in excited states of Zn_2 and molecules of other heavy atoms and also in polyatomic molecules composed of two like radicals such as C_2H_2 , C_2H_4 , C_2H_6 , N_2O_4 .

Information of a more general nature can be deduced from the above discussion. The existence of the positive, hence repulsive, limiting law even in stable states, and the large negative energy in the other cases, affords a means of discerning the London-van der Waals type of force, and distinguishing it from exchange and penetration, whereas in normal states, in particular the most important ground state, the transition of the limiting $1/r^6$ interaction into the short range interactions cannot be detected from the nature of the potential curve. Since the course of our curves, especially those of Na_2 , are fixed fairly accurately by experiment and by theory, we can make a definite observation as to the importance and extent of the London-van der Waals forces. In the cases of Cd_2 and Hg_2 the $1/r^3$ law predominates even at the equilibrium distance; in Na_2 it accounts for about 0.1 ev, but in H_2 it represents only a small fraction of the total binding energy.

In closing, we may suggest the possibility that the repulsive $1/r^3$ type of van der Waals force furnish the activation hill in, perhaps, e.g., the dimerization of NO_2 .

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²² F. London, *Zeits. f. physik. Chemie* **B11**, 222 (1930).