Evidence for such increases in the case of ions of high energy is given by Mitchel and Ridler[12] and by Ramsauer and Beeck.[13] Hence one can, assuming that the energy is gained in one free path, set the energy of the ion as about $X\lambda$, i.e., the potential existing across an ionic free path in the direction of the field. This yields 0.68 volt for $\lambda=1\times10^{-5}$ cm and 0.136 volt for $\lambda=0.2\times10^{-5}$ cm. Considering persistence of velocity and the probability that λ has begun to increase in this region the upper figure seems the more probable. Again it must be remembered that in ion impact with a molecule the total energy above is not all available for detachment for some must go to conserve momentum, which in this case means that only half of the 0.68 volt is available for detachment. Hence we can conclude that the *electron when it attaches to an* O_2 *molecule in general does not liberate much more than 0.34 electron volt of energy*. Thus the red limit of a continuous attachment spectrum would lie at 0.34 volt and since Bradbury has shown that attachment becomes small for electrons of 0.4-volt energy it is clear that a continuous electron affinity spectrum must be looked for between 36,300A and 15,800A, and it might possibly be in still longer wave-lengths. As at present there seems to be no way of accurately fixing the energy of an ion in O_2 in a field where $X/p=90$ these limits must for the present suffice.

In conclusion the writer desires to express his thanks to Mr. Fred Ludecke who was sent to him by S.E.R.A. to help in this work, and without whose assistance some of the data could not have been taken, to Dr. A. M. Cravath for his calculations of the value of the smasher field, to Professors N. E. Bradbury and O. Luhr for their valuable discussions in connection with this work and to Dr. L. C. Marshall for the design of the oscillators used.

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[12] Mitchel and Ridler, Proc. Roy. Soc. **A146**, 911 (1934).

[13] Ramsauer and Beeck, Ann. d. Physik **87**, 1 (1928).

OCTOBER 15, 1935 PHYSICAL REVIEW VOLUME 48

On the Mechanism of Unimolecular Electron Capture

FELIX BLOCH AND NORRIS E. BRADBURY, *Department of Physics, Stanford University*

(Received June 19, 1935)

The formation of negative ions by electron capture in gases in which a dissociation process does not occur is explained by a unimolecular process involving the excitation of molecular vibrational levels and subsequent loss of energy by collision or resonance. In order to obtain a proper order of magnitude to agree with experimental observations, one must assume a change of only one vibrational quantum number. This sets an upper limit on the electron affinity. For the case of O_2, this limit is 0.17 volt consistent with other observations. The theory also yields a dependence of the phenomenon on the average energy of the electrons which is in agreement with experiment.

1. INTRODUCTION

IT is an experimental fact that if a current of free electrons be sent into certain gases, a more or less rapid change in the character of the carriers of negative electricity occurs. This change is one from a high mobility and high random velocity of agitation to drift velocities a thousand-fold smaller. Such a change must be associated with a change from electronic carriers to carriers of at least molecular dimensions. There occurs, therefore, a capture process in gases wherein initially free electrons become attached to neutral molecules forming stable negative ions. The experimental aspects of this process of electron capture and negative ion formation have been studied in some detail,[1, 2] and some of the important characteristics of the phenomena may be briefly summarized.

If the capture process is a random one as the electrons drift through the gas, then a *capture*

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[1] N. E. Bradbury, Phys. Rev. **44**, 883 (1933); J. Chem. Phys. **2**, 827 (1934).

[2] V. A. Bailey, Phil. Mag. **10**, 145 (1930).

cross section, σ_c, may be defined such that the loss of free electrons in going a distance dx in the direction of the applied field is given by

$$dI = -I\sigma_c N v_0 / W dx. \qquad (1)$$

In this equation I is the free electron current, N, the number of molecules per unit volume, W the drift velocity, and v_0, the average speed of agitation. In actual practice a quantity h is often used. This is the so-called probability of capture at a collision and is defined by $h = \sigma_c/\sigma_R$ where σ_R is the Ramsauer cross section. The result of (1) is an exponential absorption of free electrons as they attach to neutral molecules thereby forming negative ions.

The quantity h varies in magnitude both with the nature of the gas and with the quantity X/p, the ratio of field strength to pressure. This latter quantity is closely related to the average energy of the electrons in the gas, and hence the probability of capture appears to be a function of the average energy of the electrons. In general one finds three widely varying types of behavior in different gases. The first of these may be characterized by the fact that no negative ion formation is observed at any electronic energy and can be explained by the absence of an electron affinity. Such cases are found in the rare gases, nitrogen, hydrogen, and CO_2. In the second case, negative ions are only formed by sufficiently high energy electrons such that dissociation of the molecule can occur. Examples of this are found in N_2O, NH_3, and HCl. Finally, there are gases in which electrons of very low velocity can be captured, and in fact show a decrease of the cross section with increasing electronic energy.

With few exceptions, the value of h seems to be largely independent of pressure for pressures greater than a few mm of Hg. There is qualitative evidence,[3] however, that the probability of capture in oxygen decreases with decrease in pressure below 2 mm, and a strong variation with pressure is observed in NO.

The general phenomena of negative ion formation in most cases are fairly well established. There remains, however, the necessity of discussing the mechanism of the capturing process. A tentative rule has been given for predicting whether or not a given molecule will possess an electron affinity.[4] Granting that this affinity exists, one has to consider the problem of the disposal of the energy which must appear when a negative ion is formed. *A priori* one may consider several possible mechanisms, such as (1) radiation; (2) dissociation; (3) molecular excitation. Let us consider these suggestions in order.

Radiation has been frequently suggested as the form of appearance of the energy. However, the cross sections for such processes have been calculated and are too small by orders of magnitude. In particular Jen[5] has calculated the cross section for capture by radiation of the hydrogen atom (for which the electron affinity is 0.7 volt) and obtains a value of 10^{-22} cm^2 corresponding to an h of the order of 10^{-7}. While this case has not been observed experimentally, the appearance of radiation energy corresponding to the sum of the electron affinity and initial kinetic energy of the electron seems exceedingly improbable.

Electron attachment and simultaneous molecular dissociation resulting in the formation of a negative ion with one of the molecular fragments is of relatively common occurrence with polyatomic molecules. In such cases the energy is carried away in kinetic form by the products of the dissociation. This type of negative ion formation is invariably associated with an increase in the probability of negative ion formation with increasing electronic energy.

This second mechanism apparently does not occur in oxygen or nitric oxide since in these gases an entirely different type of energy dependence is observed, and in addition the electron affinity cannot be as much as the approximately 6 volts necessary to dissociate the molecule. For this case, therefore, we have to consider as a process the excitation of molecular vibration and rotational levels with subsequent loss of energy to other molecules. The theoretical treatment of this means of electron capture will form the subject of this paper and will be treated in the next section.

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[3] H. L. Brose, Phil. Mag. **50**, 536 (1925).

[4] N. E. Bradbury, J. Chem. Phys. **2**, 840 (1934).

[5] C. K. Jen, Phys. Rev. **43**, 540 (1933).

2. Theory of Electron-Capture by Molecular Excitation

The capture of an electron by a transition from a free state into a bound state in the molecule and the simultaneous excitation of molecular energy levels is an effect of the weak coupling between electronic and nuclear motion. We will restrict our considerations to the case of diatomic molecules and first ask for the probability of transitions due to this coupling.

Considering the center of gravity of the molecule at rest, we will describe the interaction between electron and molecule by a potential $V(\mathbf{R}, \mathbf{r})$ depending on the position vector $\mathbf{r}$ of the electron and on the vector $\mathbf{R}$ of the relative position of the two nuclei.[6] Let k (standing for three quantum numbers) be a stationary state of the electron at a *given* relative position of the nuclei. The corresponding energy level shall be $E_k(\mathbf{R})$, the normalized eigenfunction $\psi_k(\mathbf{R}, \mathbf{r})$ and the connection between the stationary states, denoted by the same symbol k for different vectors $\mathbf{R}$ shall be that of adiabatic variation of $\mathbf{R}$. Similarly K shall denote the three quantum numbers of a stationary state of nuclear motion under the action of a potential

$$U_k(\mathbf{R}) = U_0(\mathbf{R}) + E_k(\mathbf{R}), \qquad (2)$$

where $U_0(\mathbf{R})$ is the potential of nuclear motion for the neutral molecule. The normalized eigenfunction of this state will only depend on $\mathbf{R}$ and shall be denoted by $\Psi_{K,\,k}(\mathbf{R})$, the energy level by $E_{K,\,k}$. The equations for the variation of constants will then appear in the form

$$(\hbar/i)\dot{a}_{Kk} = \sum_{K'k'} T_{Kk,\,K'k'} a_{K'k'}, \qquad (3)$$

where $|a_{Kk}|^2$ is the probability of finding the molecule in a state of electronic motion, k, and nuclear motion, K. $T_{Kk,\,K'k'}$ is the matrix element of the perturbation energy T, which can be easily seen with the above definition of stationary states K, k to be the kinetic energy of the nuclei. The function $U_k(\mathbf{R})$ can be assumed to depend only on the relative distance ξ of the nuclei.[7] Introducing, furthermore, polar angles θ, φ for the direction of $\mathbf{R}$, and calling M the arithmetic mean of the two atomic masses, we can write

$$T_{Kk,\,K'k'} = \frac{\hbar^2}{M}\int \Psi_{Kk}^*(\xi, \theta, \varphi)\psi_k^*(\xi, \theta, \varphi, \mathbf{r})\left[\frac{\partial^2}{\partial \xi^2} + \frac{2}{\xi}\frac{\partial}{\partial \xi} + \frac{1}{\xi^2}\Delta\theta\right]\psi_{k'}(\xi, \theta, \varphi, \mathbf{r})\Psi_{K'k'}(\xi, \theta, \varphi)\xi^2 \sin\theta d\theta d\varphi d\mathbf{r}, \qquad (4)$$

where

$$\hbar = h/2\pi, \quad d\mathbf{r} = dxdydz, \quad \Delta\theta = \frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$

The quantity which is physically interesting is the probability $dP_{KK'}/dt$ that an electron during unit time will make a transition from a free to a bound state associated with a transition $K-K'$ of the molecule. In order to obtain $dP_{KK'}/dt$ from (3), one has to remember that in a gas we have always to deal with a continuous velocity distribution, due to the many though small energy changes from previous collisions with molecules. This is important since going over from the probability $|a|^2$ to $dP_{KK'}/dt$ one has to integrate over a narrow energy range in the neighborhood of that energy, for which $E_{Kk} = E_{K'k'}$. The breadth of this range is given by the lifetime of the final state of the molecule,[8] and if we may assume for simplicity that only *one* bound state of the electron in the molecule is effectively important, this means that for any given molecular transition $K-K'$ only electrons with a very well defined energy can be captured at all.

If $f(E)dE$ is the probability of finding in the stationary distribution an electron within a range between E and $E+dE$ of its kinetic energy and if N is the number of molecules per unit volume one finds thus from (3)

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[6] M. Born and R. Oppenheimer, Ann. d. Physik **84**, 457 (1927).

[7] For bound states k of the electron this is, of course, true. For free states k there is a privileged direction in space, namely, the asymptotic direction of the electrons. Due to the fact that we shall deal only with slow electrons and have E_k small compared to U_0, this effect is quite negligible.

[8] The lifetime of the initial state is practically infinite.

$$dP_{KK'}/dt=(2\pi/\hbar)Nf(E^*)\,|S_{KK'}(E^*)|^2. \quad (5)$$

$S_{KK'}(E^*)$ in (5) is the same expression as $T_{Kk,\,K'k'}$ in (4) with the difference, that the electronic functions ψ_k of the initial free state are normalized per unit volume and that k has to be taken such that $E_{Kk}=E_{K'k'}$. E^* shall be the kinetic energy of the free electron for which this condition is fulfilled and to replace the index k in (4), we have written $S_{KK'}$ as a function of E^*. The index k' has been omitted with the understanding that it shall always be taken as the symbol, representing the final bound state of the electron. The expression (5) depends then only on K and K' since E^* is also determined by K and K' through the relation $E_{Kk}=E_{K'}{}_{k}{}'$.

Instead of the quantity (5) we will introduce the capture cross section σ_c from (1) by the relation

$$dP_{KK'}/dt=v_0(\sigma_c)_{KK'}N,$$

or
$$(\sigma_c)_{KK'}=(2\pi/\hbar v_0)f(E^*)\,|S_{KK'}(E^*)|^2. \quad (6)$$

$$v_0=\int_0^\infty(2E/m)^{\frac{1}{2}}f(E)dE$$

is the average speed of the electron.

Without knowing more about the electronic eigenfunctions, than that in the bound state the electron will be found within a volume of the molecular dimensions, we can tell from the order of magnitude of σ_c as given by (6) and (4), which excited states K' of the molecule are most likely to occur and how σ_c is affected by the magnitude of the electron affinity.

Instead of the symbol K we will now use three quantum numbers l, m, n, where $l\hbar$ is the angular momentum, m the azimuthal quantum number, and n the number of quanta of the oscillation of the nuclei around their equilibrium position. Ψ_K in (4) is then a product of a tesseral harmonic of the order l, depending on θ and φ and a function of ξ, being very closely the eigenfunction of the nth state of the harmonic oscillator. Unless the de Broglie wave-length of the incident electron is short compared with molecular dimensions, the expansion of ψ_k and $\psi_{k'}$ with respect to their dependence on θ and φ in tesseral harmonics will practically contain only the first few orders; changes of l by a large number are thus most unlikely. Capturing by mere *rotational* excitation could therefore only occur if the electron affinity were of the order of magnitude of the separation of two rotational levels. But at room temperature this would be less than kT and negative ions so formed would be thermally instable. Therefore the main part of the capturing mechanism must lie in *vibrational* excitation. We may for further purposes assume that no changes of l occur at all; we have then merely to remember, that all energy considerations used later on are only valid with an approximate error of the order of magnitude of the ratio of the separation of rotational and vibrational levels, i.e., about 1 percent.

As far as vibrational excitations are concerned, only those terms under the integral (4) contribute that contain derivatives of $\psi_{k'}$; the others vanish due to the orthogonality of ψ_k and $\psi_{k'}$ with respect to the electron coordinates. Among the remaining terms again, those with *first* derivatives in ξ both of $\psi_{k'}$ and $\Psi_{Kk'}$ will prevail. In fact they will stand to those with the second derivatives of ψ_k in the approximate ratio a/δ, where a is a length of the order of molecular dimensions, and δ the amplitude of the vibration. This is due to the fact that each differentiation, with respect to ξ, acting on $\psi_{k'}$ will give a new factor $1/a$ in the expression (4), since $\psi_{k'}$ both as function of $\mathbf{r}$ and ξ varies essentially over regions of molecular magnitude, while $\Psi_{K'k'}$ as function of ξ will essentially vary over the much smaller region δ. This means physically, that the velocity of the nuclear motion will be so much smaller than that of the electron in its bound state that only terms linear in the nuclear velocity have to be considered. In order to see the dependence of σ_c on the number of excited quanta, it is convenient to expand $\psi_k^*\partial\psi_{k'}/\partial\xi$ in terms of $\Delta\xi=\xi-\bar{\xi}$ around the equilibrium position $\bar{\xi}$ of the two nuclei. Due to the selection rules of the harmonic oscillator, changes of n by the amount $n'-n=\Delta n$ can only occur by terms with at least the $(\Delta n-1)$ power in $\Delta\xi$. But each following power of $\Delta\xi$ diminishes the expression (4) by a factor of the order of magnitude δ/a. At room temperature there will practically be no thermal vibrational excitation, thus $n=0$. Neglecting the dependence of S on E^* (which is certainly justified for sufficiently slow electrons) and taking into account also that ψ_k^* will not vary rapidly within nuclear dimensions, one obtains from (6) and (4) for capturing by excitation of the vibrational level n'

$$(\sigma_c)_{n'} = \alpha_{n'} \frac{m}{M} \frac{A^2a^3}{\hbar v_0} \left(\frac{\delta}{a}\right)^{2(n'-1)} f(E^*) \qquad (n'=1,\,2,\,\cdots), \quad (7)$$

where $\alpha_{n'}$ is a numerical constant of the order of magnitude 1, m, the mass of the electron, and A the electron affinity. The quantity a is connected with A by the equation $\hbar^2/2ma^2 = A$ and will be of the order of magnitude of the orbital dimensions of the electron in its bound state, i.e., of molecular dimension. This follows from the fact that the binding energy A and the average kinetic energy may be assumed as being of the same order of magnitude. δ^2 is the mean square of the elongation in the ground state of the nuclear oscillation. Formula (7) gives of course only the right order of magnitude for σ_c, if n' is of the order of magnitude 1.

Since E^*+A is the total energy, lost by the electron in the capturing process and has to be equal to the increase of vibrational energy, we have

$$E^* = n'\hbar\omega - A, \quad (8)$$

where ω is the circular frequency of the oscillation. This quantity must be positive, which means

$$A = n'\hbar\omega - E^* \leqq n'\hbar\omega \quad (9)$$

and gives us an upper limit for the electron affinity A, provided that we can determine n'. We will see in section 3 that this indeed is possible with the help of (7), although this formula tells us only the order of magnitude of σ_c. In fact the smallness of δ/a changes the order of magnitude of σ_c, even for values of n' that differ only by one.

Before going over to the discussion of the empirical results, an important supplementary consideration has to be given. The transition probability (5) does not necessarily mean the probability of a capturing process resulting in a stable ion. After the transition $Kk \rightarrow K'k'$ has occurred, the inverse transition $K'k' \rightarrow Kk$ will always occur unless during the lifetime θ of the excited ion it has had a possibility of transferring its vibrational energy to another molecule in the gas, thus becoming energetically stable. In order to have expression (7) really represent the capturing cross section, it is necessary that the transfer of vibrational energy occur during a time τ, which is short compared to the lifetime θ. Whether this is true or not depends of course on the pressure and temperature of the gas. If $\bar{v}$ is the average velocity of the molecules in the gas and s an effective cross section for transfer of vibrational energy, we have

$$\tau = 1/N\bar{v}s = \gamma/P, \quad (10)$$

where γ depends only on the temperature and p is the pressure of the gas. On the other hand, the lifetime θ of the excited ion is pressure independent and given by

$$\theta_{KK'} = 2\pi\hbar^4/(2m)^{\frac{3}{2}}(E^*)^{\frac{1}{2}}|S_{KK'}(E^*)|^2.$$

Using the same approximations as for obtaining formula (7), we obtain

$$\theta_{n'} = \frac{(2\pi)^2\hbar^4}{(2m)^{\frac{3}{2}}(E^*)^{\frac{1}{2}}\alpha_{n'}A^2a^3} \frac{M}{m} \left(\frac{a}{\delta}\right)^{2(n'-1)}, \quad (11)$$

which is the lifetime of an ion with vibrational excitation n', before a spontaneous emission of the electron occurs. The condition for the validity of (7) is

$$\theta_{n'} \gg \tau \quad (12)$$

and will be satisfied for different pressure ranges in different gases. It should be noticed that in this case the broadening of the final level of the excited ion, mentioned before, will be mostly due to transfer collisions with other molecules and of the order of magnitude $\hbar/\tau$.

On the other hand, for sufficiently low pressures, one will always come to a region where (12) is no longer satisfied and then the capturing cross section will become pressure dependent. We can give an approximate formula of this dependence by the following simple consideration: Suppose that we know at a given time $t=0$ that the ion is in its excited state, due to a previous electron transition. The probability of having it still in this state after a time t will be given by $e^{-t/\theta}$. On the other hand the probability of making a transfer collision after a time between t and $t+dt$ has elapsed is given by

$e^{-t/\tau}dt/\tau$. The total probability therefore that an excited ion makes a transfer collision is

$$\rho = \int_0^\infty e^{-(t/\theta + t/\tau)}dt/\tau = \theta/(\theta+\tau),$$

or since τ is inversely proportional to the pressure p

$$\rho = p/(p+p'), \tag{13}$$

where p' is a "critical pressure," for which $\theta=\tau$. Expression (7) has to be multiplied by this factor in order to give the cross section both for high and low pressures. We find finally:

$$(\sigma_c)_{n'} = \alpha_{n'}\frac{m}{M}\frac{A^2a^3}{\hbar v_0}\left(\frac{\delta}{a}\right)^{2(n'-1)} f(E^*)\frac{p}{p+p'}. \tag{14}$$

For $p \gg p'$ this approaches the pressure independent value (7); for $p \ll p'$, σ_c becomes a linear function of the pressure.

3. Comparison with Experiment

In order to compare the theoretical predictions given in the last section with experiment we will first obtain the value of the quantity h, introduced in section 1 that has to be expected. In order to do this we have to assume something about the Ramsauer cross section σ_R since it is not measured for these low velocities. We will expect for sufficiently low velocities that σ_R approaches some constant value of the order of magnitude a^2. This is consistent with the assumption made in section 2, that for low velocities and inside the molecule the wave function of the electron in its initial state will no longer depend on the velocity. Thus we get from (14)

$$h_{n'} = \frac{(\sigma_c)_{n'}}{\sigma_R} = \beta_{n'}\frac{m}{M}\frac{A^2a}{\hbar v_0}\left(\frac{\delta}{a}\right)^{2(n'-1)} f(E^*)\frac{p}{p+p'}, \tag{15}$$

where β' is a new numerical constant, also of order of magnitude one.

The observed order of magnitude of h for O_2 in the pressure independent region is 10^{-4} and we can see now which values of n' would yield such a result. For simplicity we will assume all the energies A, E^*, and E_0 to be of the same order of magnitude. We shall see presently that this is a reasonable assumption. The quantity $f(E^*)$ in (15) will then become of the order of magnitude $1/E_0$. The pressure dependent factor in (15) has here to be taken unity and we get

$$h_{n'} \cong (m/M)(\delta/a)^{2(n'-1)}. \tag{16}$$

Now obviously $m/M = 0.33\times 10^{-4}$ and therefore in order to have (16) of the right order of magnitude, $(\delta/a)^{2(n'-1)}$ must be of the order of magnitude one. On the other hand, δ/a will be about 1/10 and thus the only value of n' which we can admit is $n'=1$, irrespective of the fact that we can compute only the order of magnitude of h. From this we can immediately draw a conclusion as to the upper limit of the electron affinity. In fact from (9) it follows with $n'=1$

$$A = \hbar\omega - E^* \tag{17}$$

and

$$A \leqq \hbar\omega = 0.19 \text{ ev.} \tag{17a}$$

The numerical value in this inequality is taken from the well-known frequencies of the vibrational bands of the O_2 molecule.[9]

Since we now know n' to be one, we can give a final expression for h, namely,

$$h = \beta\frac{m}{M}\frac{A^2a}{\hbar v_0}f(E^*)\frac{p}{p+p'}. \quad \beta \cong 1. \tag{18}$$

Aside from the order of magnitude, (18) gives us a definite answer as to the way in which h depends upon the average energy E_0 of the electrons, if the distribution function $f(E)$ is known. The *velocity* distribution function will be of the type $v^2F(E/E_0)$ where F will approach a finite value for small arguments and rapidly drop off for large arguments. Morse has recently

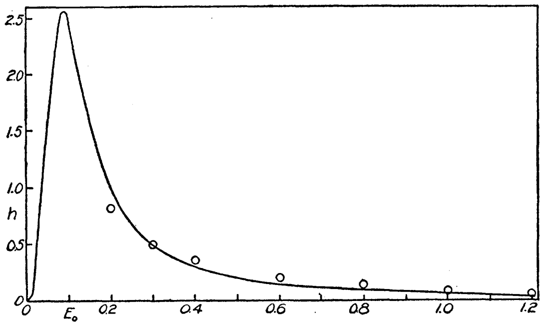

FIG. 1. Probability of capture, h (in arbitrary units) plotted against average electron energy E_0. The circles are experimental points for O_2; the full line, the theoretical curve for $E^*=0.08$ volt corresponding to an electron affinity of 0.11 volt.

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[9] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

shown that $F(E/E_0)$ has the form $F(E/E_0) = e^{-b(E/E_0)^2}$ with $b=0.847$. We will use this function, although its particular form does not materially influence our results. For the *energy* distribution function $f(E)$ we obtain then

$$f(E) = \text{const. } (E^{\frac{1}{2}}/E_0^{\frac{3}{2}})e^{-b(E/E_0)^2}. \qquad (19)$$

The factor $E_0^{\frac{3}{2}}$ in (19) has to appear since $\int_0^\infty f(E)dE=1$. Using (18) and (19) we find for the dependence of h on E_0,

$$h \alpha e^{-b(E^*/E_0)^2}/E_0^2. \qquad (20)$$

In Fig. 1 we have computed such a curve which has been adjusted for $E_0=0.3$ volt, and shown thereon the experimental points. These lie gratifyingly close to the computed curve. There, however, seems to be a systematical deviation in the sense that the theoretical curve rises somewhat too rapidly. This lies probably in the circumstance that we have chosen both for σ_c and σ_R a behavior which they would exhibit in the limit of small velocities. This behavior may not be quite reached at the velocities in which we are interested. The value of E^* which one uses does not greatly influence the character of the curve, particularly for high values of E_0. However, the very fact that there is no experimental indication of h approaching a maximum even for the smallest measured values of E_0 permits the conclusion that E cannot be bigger than about 0.12. Thus from (17) we find also a lower limit for the affinity and we can write $0.07 < A < 0.19$ electron volt. This may be at once compared with some results of Loeb[10] who finds the electron affinity of the oxygen molecule to be definitely smaller than 0.34 volt, in interesting agreement with our requirements.

It is understandable, moreover, why the measurements in O_2 above 3 mm pressure already lie in the pressure independent region. The requirement for such a behavior as stated in section 2 is $\theta \gg \tau$. Taking (11) for $n'=1$, and estimating its order of magnitude in the same manner as was done for h, we obtain $\theta \leqq 10^{-10}$ sec. If we would take in (10) for s the values of the cross section as observed in ion mobilities, we would find $\tau \leqq 10^{-9}$ sec.[11] This indicates that s has to be 10–100 times the collision cross section of the unexcited ion in order to have the requirements fulfilled. Now one has to consider that transfer of vibrational energy from one molecule to another will occur by resonance, even if they are separated by a distance considerably greater than their linear dimensions. This value of s is therefore a most reasonable one.

One must further note that for air at pressures of several mm, one does not yet observe a pressure dependence.[12] This is entirely compatible with the values of s above, although the relative number of other oxygen molecules with which the resonance condition is fulfilled is five times less than in pure O_2. Moreover, for very low pressures in oxygen there are qualitative indications of a decrease in the value of h, as must be expected from this theory. Such a behavior should also occur in air at somewhat higher pressures, but measurements in the region of low pressures are extremely difficult and have not been carried out.

Nitric oxide is the other diatomic gas observed which shows a dependence of h on E_0 similar to oxygen. Since the qualitative conditions for electron capture by molecular excitation will not be very different from those of oxygen, it is very likely that the same explanation will hold. In a similar fashion as in oxygen one may restrict the electron affinity to values less than the energy of the first vibrational level, 0.24 ev, and greater than 0.07 volt. It is interesting to notice that here the experiment *does* show a strong pressure dependence. A difference merely in quantitative conditions between NO and O_2 will be sufficient to cause a change in the ratio θ/τ large enough such that for one case the pressure dependence is hardly observable while in the other case it is strongly pronounced.

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[10] L. B. Loeb, unpublished results. We are indebted to Professor Loeb for communicating the results of his experiments to us in advance of publication.

[11] This is reasonable in view of the well-known shortening of the mean free path of an ion due to its charge.

[12] A. M. Cravath (Phys. Rev. **33**, 605 (1929)) has observed a pressure dependence in air. The effect was not observed by one of the authors nor by V. A. Bailey, and it is probable that the dependence observed was the result of some experimental peculiarity.