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A Note on the Significance of Appearance Potentials of Ions in a Mass Spectrometer

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The significance of appearance potentials determined by the two common methods is treated with the aid of some simplifying assumptions. Arguments favoring the general use of the more commonly used method are given, and it is pointed out that the initial part of the appearance potential curve of an ion cannot generally lead to unambiguous conclusions concerning the nature of the ionic state involved in the production of the ion.

I. INTRODUCTION

TWO methods have been used for determining appearance potentials of ions from their appearance-potential curves (plots of ion current *versus* energy of the ionizing electrons) obtained on the mass spectrometer or simpler critical potential apparatus. One method takes as the appearance potential of an ion the corrected electron energy corresponding to the first detectable ion current; for want of a better name, and for the sake of brevity, this will be called the vanishing-current or VC method. The other method, which will be referred to as the linear-extrapolation or LE method, takes as the appearance potential of an ion the corrected electron energy corresponding to the energy intercept of the extrapolated linear part of the appearance-potential curve. Both methods have been used since early in the history of electron impact studies;* but use of the LE method has been relatively rare. In a recent paper,[1] however, the LE method has been used again, and the interesting observation has been made that its application to a fragment ion of a molecule gives, under certain conditions, quite closely the energy required for a transition through the center of the Franck-Condon region. It has also been implied that the LE method gives energies standing in a more definite relationship with the physical quantities involved than does the VC method. Since we are not in full agreement with this implication, nor with the statements of the reference paper with regard to the principal limitation of the VC method, nor with the statement of conditions under which the LE method gives quite closely the transition energy in the center of the Franck-Condon region, and since we feel that there are arguments favoring the general use of the VC method, we should like to present our views on the significance of appearance potentials obtained by the two methods. None of our remarks is to be construed as criticism of the treatment of dissociation processes in $SiCl_4$ discussed in the reference paper.

We have chosen to use a mathematical symbolism in presenting the following discussion, since it seems to be the briefest and clearest way of emphasizing the relationships between the various factors which are known to influence appearance-potential measurements. We are well aware of the departure from quantitative rigorousness which results both from over-simplification of assumptions concerning the nature of the ionization process itself and from complete neglect of the effect of variable instrumental efficiency;[2] and we do not wish to imply that the derived expressions will be generally useful in a quantitative way. However, by giving a direct and easily understandable approach to the qualitative relationships which must be taken

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* For some early examples of the VC method, see Hogness and Lunn, Phys. Rev. **26**, 44 (1925); H. D. Smyth, Phys. Rev. **25**, 452 (1925); W. Bleakney, Phys. Rev. **36**, 1303 (1930); and for some early examples of the LE method see, P. T. Smith, Phys. Rev. **36**, 1293 (1930); P. T. Smith and J. T. Tate, Phys. Rev. **39**, 27 (1932); Tate, Smith, and Vaughan, Phys. Rev. **48**, 525 (1935).

[1] R. H. Vought, Phys. Rev. **71**, 93 (1947).

[2] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

into account in formulating decisions concerning the best method of handling electron impact data, we believe that the simplified treatment is adequately justified.

II. DISCUSSION

General Significance of VC Appearance Potentials

In application of the VC method appearance-potential curves are plotted both for the ion whose appearance-potential is to be determined and for the ion whose appearance potential is known (usually the ion of a monatomic gas, such as argon, the ionization potential of which has been determined spectroscopically). For both appearance-potential curves the nominal electron energy corresponding to the first detectable ion current is determined. The difference between the nominal energy for the experimental ion and that for the calibrating ion is added to the known appearance potential of the calibrating ion to give the corrected appearance potential of the experimental ion.

It is not possible to give a precise answer to the question of the significance of an appearance potential obtained by the VC method; but general considerations lead to an interpretation which is not inconsistent with the generally satisfactory results which have been obtained by use of the method.[2-4] In the case of the calibrating atomic gas (let us consider argon, to be specific), and under conditions of reasonably high sensitivity, the first detectable ion current probably appears when the most energetic group of electrons of significant intensity in the Maxwellian distribution have just enough energy to cause a transition to the ${}^2P_{1\frac{1}{2}}{}^0$ state of A^+. The actual trend of the ionization curve after the onset of ionization will (apart from the unknown factors in the trend of the ionization cross section) depend on both the influence of the low lying ${}^2P_{\frac{1}{2}}{}^0$ state of A^+ and the finite spread of electron energies;[4] but we are concerned only with the region very close to onset of ionization. It may be that the curve should approach the energy axis asymptotically; but with sufficiently high sensitivity it appears to have a reasonably large slope even over the first 0.2 volt after the apparent onset of ionization, which it seems to be possible to locate to within about 0.05 volt (see Fig. 1 of the preceding paper). Thus, under conditions of high sensitivity, the part of the curve which is important for determination of the VC appearance potential is probably produced by electrons in a fairly narrow energy band, namely, the most energetic group of electrons which have significant intensity in the energy distribution. In the case of an ion produced from a molecule, the trend of the appearance-potential curve after the onset of ionization will be influenced by the spread of electron energies, by the distribution of vibrational levels in the ionized state, by the shape and position of the potential function of the ionized state relative to the normal state, by the existence of neighboring states involving the ion in question, and by the shape of the expectation function of the ground level, in addition to unknown factors. However, when the sensitivity is so high that the appearance-potential curve has a reasonably high slope over the first few tenths of a volt after the apparent onset of ionization (see Fig. 4 of the preceding paper), it seems reasonable to believe that the part of the curve in which we are interested is due to the same narrow energy band of electrons considered for the atomic ion, and that the first detectable ion current appears when the energy of this group of electrons is just sufficient to effect the least energetic transition (between the ground level and the ionic state in question) among the possible vertical transitions which correspond to significant values of the expectation function of the ground level. Since the same group of electrons in a narrow band at the high energy end of the electron energy spectrum is probably responsible for onset of ionization in both the calibrating gas and the experimental gas, it seems that the finite spread in electron energies should have practically no influence on VC appearance potentials when reasonably high sensitivity is used for both the calibrating ion and the experimental ions. At lower sensitivities a broader band of electron energies is effective at the apparent onset of ionization; but the effect of this broader band is probably largely accounted for in the increased estimate of experi-

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[3] For example, see D. P. Stevenson and J. A. Hipple, Phys. Rev. **62**, 237 (1942).

[4] W. Bleakney, Phys. Rev. **40**, 496 (1932).

mental error which follows as a consequence of poorer definition of the point of onset of ionization at lower sensitivities. In any case, the effect of the finite spread in electron energies does not constitute the chief objection to the VC method. The chief objection is that the observed appearance potential, corresponding to the least energetic observable transition as described above, does not generally correspond to the energy difference between the lowest level of the ionized state in question and the lowest level of the ground state. If this limitation did not exist, there would probably be (apart from possible uncertainty in the electronic excitation) no discrepancy between VC electron impact data, on the one hand, and ionization potentials and dissociation energies obtained spectroscopically and thermochemically on the other hand.

General Significance of LE Appearance Potentials

For consideration of the significance of an appearance potential determined by the linear-extrapolation method it is convenient to make use of some simplifying assumptions which are not strictly correct; but they are probably not so extreme as to invalidate the analysis of the relationship of the various factors which influence an LE appearance potential. In the case of the ionization potential of an atom we will use in particular the basic assumption used recently by Vought[1] and earlier by others,[5] and indicated by the work of Stevenson and Hipple[3] to be not strictly correct near the critical potentials, namely, that the probability of ionization by electrons of energy $E_e > E_0$ is proportional to the difference $E_e - E_0$, where E_0 is the ionization potential. Let the distribution of electron energies be such that the number of electrons per second with energy E_e is given by $n_e = n_0 \cdot f_1(E_e - {}^0E_e)$, where n_0 is the number per second with the most probable energy ${}^0E_e$. Then the electrons in the energy interval dE_e near $E_e > E_0$ will, by causing ionization to the ${}^2P_{1\frac{1}{2}}{}^0$ state of ionized argon, say, produce an ion current:

$$I_1 = ck_1 \cdot (E_e - E_0) \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot dE_e.$$

If we designate by α the energy difference between the ${}^2P_{\frac{1}{2}}{}^0$ and ${}^2P_{1\frac{1}{2}}{}^0$ states of the ionized atom, then electrons in the energy interval dE_e near $E_e > E_0 + \alpha$ will also, by causing ionization to the ${}^2P_{\frac{1}{2}}{}^0$ state of the ionized atom, produce an additional ion current:

$$I_2 = ck_2 \cdot (E_e - E_0 - \alpha) \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot dE_e.$$

In these equations c is the instrumental sensitivity factor, which is really unimportant in this treatment, and k_1 and k_2 are the relative probabilities of the two processes under equally favorable energy conditions. When all the electrons have sufficient energy to cause ionization to either level, the total ion current at a particular ${}^0E_e$ will be given by:

$$I_t = c(k_1 + k_2) \int \left(E_e - E_0 - \frac{k_2 \alpha}{k_1 + k_2} \right) \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot dE_e.$$

Writing $(E_e - {}^0E_e) + ({}^0E_e - E_0)$ for $(E_e - E_0)$, we obtain:

$$\frac{I_t}{c(k_1 + k_2)} = \int (E_e - {}^0E_e) \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot dE_e + \int \left({}^0E_e - E_0 - \frac{k_2 \alpha}{k_1 + k_2} \right) \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot dE_e.$$

If N is the total number of electrons per second, then the first integral becomes NA_e, where A_e is the average algebraic deviation of electron energy from the most probable electron energy; and the second integral is easily integrable, so that for sufficiently high electron energies we get the expression,

$$\frac{I_t}{c(k_1 + k_2)} = N \left({}^0E_e - E_0 - \frac{k_2 \alpha}{k_1 + k_2} + A_e \right),$$

which is linear in the most probable electron energy ${}^0E_e$. Linear extrapolation to $I_t = 0$ puts a condition on the most probable electron energy, namely,

$$ {}^0E_e{}^a = E_0{}^a + \frac{k_2 \alpha}{k_1 + k_2} - A_e, \qquad (1)$$

where the superscript, a, on the electron energy and ionization potential is an index to distinguish them from corresponding quantities in the subsequent discussion of an ion produced from a molecule. In practice the most probable electron energy is not measured directly, because of con-

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[5] H. D. Smyth, Phys. Rev. **25**, 452 (1925).

tact potentials and other instrumental factors. What is measured is the nominal electron energy ${}^sE_e$, which differs from the most probable electron energy by an instrumental constant Q. Thus, the expression for the apparent LE appearance potential of an ion produced from a rare gas becomes

$$ {}^sE_e{}^a = E_0{}^a + \frac{k_2}{k_1+k_2} - A_e - Q. \qquad (1a)$$

Equation (1a) shows that the apparent LE ionization potential of a rare gas is influenced by the multiplicity of the lowest state of the ion as well as by asymmetry in the distribution of electron energies.

For the treatment of the LE appearance potential of an ion produced from a molecule we will speak in terms of a diatomic molecule for the sake of simplicity; but it will be clear that the results are more generally applicable. Let the ground level of the molecule be described by an expectation function such that $R_i = R_0 \cdot f_2(r_i - r_0)$ is the probability that the molecule has the internuclear distance r_i, where R_0 is the probability of occurrence of the most probable internuclear distance, r_0. Let the energy of a transition from the ground level of the molecule to the level of the ionic state which intersects the ionic state potential function at r_0 be E_0. Then the energies of transition to the other levels of the ionic state can be represented by $E_i = E_0 + f_3(r_i - r_0)$. We will assume the same type of dependence of transition probability on electron energy and the same electron energy distribution that we assumed in the case of ionization of a rare gas. In addition, we will assume, to a fairly good degree of approximation for unstable ionic states and to a sufficiently good degree of approximation for stable ionic states, that transitions occur from the ground level of the molecule only to the potential function of the ionic state itself, and that so far as the effect of the upper levels is concerned, all such possible transitions are equally probable under equally favorable energy conditions.

For unstable ionic states, the last assumption will be recognized as the same sort of approximation to the Franck-Condon principle as that introduced by Condon in one of his early papers.[6] It is equivalent to replacing the wave functions of the vibrational levels of the unstable ionic state by δ-functions of equal value at the turning points, so that the dependence of transition probability on the square of the overlap integral is reduced to dependence on the square of the wave function of the stable initial level. This approximation has been used frequently and has been shown by Coolidge, James, and Present[7] to yield results as satisfactory as strict application of the Franck-Condon principle in the case of some particular transitions in hydrogen. Of special interest is the fact that Hagstrum and Tate[2] have applied the approximation in successfully treating the contours of beams of ions produced in dissociation of diatomic molecules by electron impact, their function $(\psi_L)^2$ being equivalent to our R_i. It should be noted that the cited papers have dealt with cases in which one state was wholly unstable for the transitions considered. Application of the approximation to stable states, as done in the present paper, is not so well justified; but it is certainly good enough to lead to the proper qualitative conclusions.

Proceeding on the basis of the stated assumptions, it is clear that the ion current produced by electrons in the energy interval dE_e near $E_e > E_i$ as the result of their impact on molecules with internuclear distances in the interval dr_i near r_i will be given by

$$dI = ck[E_e - E_0 - f_3(r_i - r_0)] \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot R_0 \cdot f_2(r_i - r_0) \cdot dr_i \cdot dE_e.$$

Writing $(E_e - {}^0E_e) + ({}^0E_e - E_0)$ for $(E_e - E_0)$, we get for the total current of the particular ion at high electron energies:

$$\begin{aligned} \frac{I_t}{ck} = & \int\int (E_e - {}^0E_e) \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot R_0 \cdot f_2(r_i - r_0) \cdot dr_i \cdot dE_e \\ & + \int\int ({}^0E_e - E_0) \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot R_0 \cdot f_2(r_i - r_0) \cdot dr_i \cdot dE_e \\ & - \int\int f_3(r_i - r_0) \cdot n_0 \cdot f_1(E_e - {}^0E_e) \cdot R_0 \cdot f_2(r_i - r_0) \cdot dr_i \cdot dE_e. \end{aligned}$$

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[6] E. U. Condon, Phys. Rev. **32**, 858 (1928).

[7] A. S. Coolidge, H. M. James, and R. D. Present, J. Chem. Phys. **4**, 193 (1941).

Performing the integrations over the whole range of electron energies and over the range of internuclear distances appropriate to the ionization and dissociation process in question we get $I_t/Bck = N(A_e + {}^0E_e - E_0 - A_r)$, where N is the total number of electrons per second; A_e is the average algebraic deviation of the electron energy from the most probable electron energy, ${}^0E_e$; E_0 is the energy of the most probable transition; B is equal to $\int R_0 \cdot f_2(r_i - r_0) \cdot dr_i$ over the range of internuclear distances appropriate to the process; and A_r is the average algebraic deviation of energies of possible transitions (within this same range of internuclear distances) from the energy of the most probable transition, the transitions being weighted according to the expectation function of the ground level of the molecule.** The expression for the total ion current is thus linear in the most probable electron energy at high electron energies; and linear extrapolation to zero current requires that

$$ {}^0E_e^m = E_0^m + A_r - A_e, \tag{2} $$

which, in turn, as in the case of Eq. (1a), leads to an expression for the apparent LE appearance potential:

$$ {}^sE_e^m = E_0^m + A_r - A_e - Q. \tag{2a} $$

(The superscript, m, in the last two equations identifies the quantities as referring to the production of an ion from a molecule.) In practice, the difference between (2a) and the apparent LE ionization potential of a rare gas given in (1a) would be added to the known ionization potential of the rare gas to get the corrected appearance potential of the ion produced from the molecule. Performing these operations, we get for the corrected LE appearance potential of an ion produced from a molecule the value:

$$ \text{A.P.}(X^+) = E_0^m + A_r - \frac{k_2\alpha}{k_1 + k_2}. \tag{3} $$

It is to be noted, contrary to the implications of reference 1, that the asymmetry in the electron energy distribution does not influence the corrected appearance potential, inasmuch as the effects are equal for both the calibrating ion and the experimental ion. Thus the effects of curvature of the potential function of the ionized state in the Franck-Condon region and the effects of asymmetry of the expectation function of the initial state of the molecule remain in full measure, since both sets of effects are contained in A_r. In addition, the significance of LE appearance potentials is affected by the multiplicity of the lowest state of the ion of the rare gas used for calibration. To estimate the order of magnitude of the error introduced by neglect of the latter effect we can probably take the k's to be simply proportional to the quantum weights of the corresponding levels, since the last term in (3) is not extremely sensitive to the k's. Since α is 0.178 volts for argon,[8] the error would be about 0.06 volt when argon is used for calibration. If krypton, for which α is 0.67 volt,[8] is used for calibration, the error would be about 0.22 volt. It is desirable to note that consideration of the effect of multiplicity will probably not alter the conclusion of Stevenson and Hipple[3] with regard to the validity of the assumption of linear dependence of ionization probability on electron energy, since the discrepancy which they find between the true difference in the ionization potentials of neon and argon and the difference in the LE values will be reduced by only 0.03 volt.

Because of uncertainty in the second term in the expression (Eq. (3)) for an appearance potential determined by the linear-extrapolation method and of lack of precise knowledge concerning the details of the ionization process for electron energies near the critical potentials,[3] it can hardly be said that LE appearance potentials have a more definite physical significance than VC appearance potentials. There is a difference in significance, however, in that the LE appearance potentials correspond generally to a higher degree of vibrational excitation in the ionized state than do the VC appearance potentials. Thus the chief objection to the VC method is applicable in greater measure to the LE method. Another consideration favoring the VC method is that appearance potential curves for

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** It will be observed that this treatment implies an essentially continuous distribution of levels for a stable ionic state as well as for an unstable one. Considerable simplification is gained in this way without impairing the qualitative conclusions.

[8] Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

some ions do not become straight within a reasonable range of electron energies,[9] thus making application of the LE method impossible. Moreover, if an ion arises in two processes requiring energies so nearly the same that the appearance potential curve does not become straight before the onset of the more energetic process, the possibility of there being a second appearance potential may easily be missed if the LE method is applied, and the single value of appearance potential obtained by that method will not correspond to the value for either process, but rather to some intermediate value.

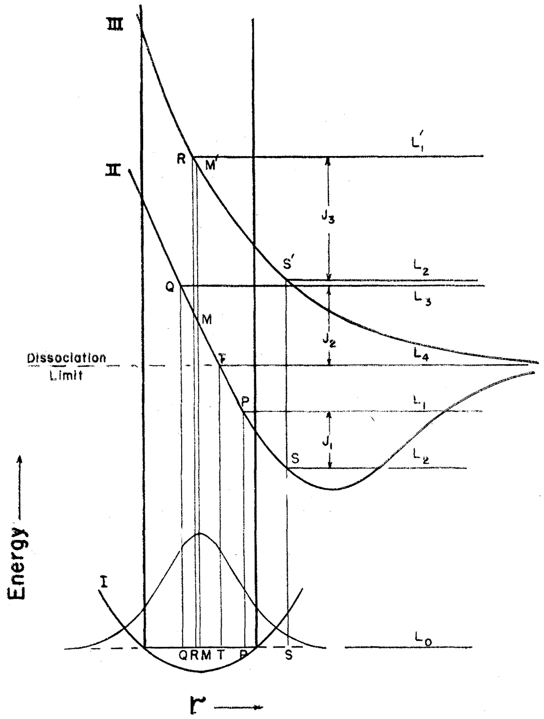

FIG. 1. Some hypothetical potential functions showing the approximate significance of corrected appearance potentials:

I	normal state of a hypothetical molecule.
II	stable ionic state of the molecule.
III	unstable ionic state of the molecule.
MM	energy of most probable transition between *I* and *II*.
MM'	energy of most probable transition between *I* and *III*.
SS	approximate *VC* appearance potential of molecular ions.
PP	the corresponding *LE* appearance potential $+k_2\alpha/k_1+k_2$.
TT	approximate *VC* appearance potential for fragment ions produced by transition to state *II*.
QQ	the corresponding *LE* appearance potential $+k_2\alpha/k_1+k_2$.
SS'	approximate *VC* appearance potential for fragment ions produced by transition to state *III*.
RR	the corresponding *LE* appearance potential $+k_2\alpha/k_1+k_2$.

Significance of the Difference between the LE and VC Appearance Potentials of an Ion

For a discussion of the possibility of deriving information concerning the configuration of the potential functions of the ionic states of a molecule from an investigation of the "feet" of the appearance-potential curves (i.e., the difference between the apparent LE and VC appearance potentials) we must first know the significance of the difference between the values of ${}^sE_e$ (or, alternatively, of ${}^0E_e$) which correspond to the LE and VC ionization potentials of the calibrating gas, since it is only by subtracting this difference from the corresponding difference for an ion produced from a molecule that we can make an approximate correction for the spread in electron energies and arrive at a quantity which we may hope to be related primarily to a potential function of an ionic state of the molecule. For the atomic calibrating ion the LE appearance potential corresponds to a particular condition for the most probable electron energy, which has already been stated in Eq. (1). The VC appearance potential, on the other hand, corresponds to a particular condition for ${}^hE_e$, the mean energy of the narrow energy band in which fall the first group of high energy electrons occurring in significant intensity in the electron energy distribution. This condition is that ${}^hE_e = E_0{}^a$, which, however, can be converted to a condition for the most probable electron energy, since ${}^hE_e$ is some definite energy, H, above ${}^0E_e$. The condition for ${}^0E_e$ corresponding to the VC appearance potential can thus be written ${}^0E_e{}^a = E_0{}^a - H$. The difference between the expression in Eq. (1) and this expression gives the energy interval between points corresponding to the VC and LE appearance potentials on the energy axis of the appearance-potential curve. This interval, which we will call the span, has then, for the calibrating ion, the value:

$$\text{span}_1 = \frac{k_2\alpha}{k_1+k_2} + H - A_e. \tag{4}$$

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[9] For example, see the curve for H^+ from methane; L. G. Smith, Phys. Rev. 51, 265 (1937).

To help in interpreting the significance of the span for an ion produced from a molecule some hypothetical potential functions have been drawn in Fig. 1. Curve *I* is for the stable normal state of a hypothetical diatomic molecule, whose lowest vibrational level is L_0. The bold vertical lines represent the classical limits of vibration or the commonly accepted limits of the Franck-Condon region. The expectation function for the lowest level has been drawn schematically. Curves *II* and *III* represent stable and unstable ionic states, respectively. The potential functions *I*, *II*, and *III* are not intended to represent those of any real molecule, although, with certain features exaggerated, they are similar to potential functions for H_2 and H_2^+;[10] and the placement of levels in the figure is very rough, since that is all that is necessary for the subsequent discussion.

Let us consider transitions between the normal state and the stable ionic state represented by curve *II*. It is evident that such transitions can give rise to either a molecular ion or an atomic ion depending on the initial nuclear separation. We shall discuss first the molecular ion arising from transitions lying on the right of *TT*. The condition on ${}^0E_e$ corresponding to the LE appearance potential is given by Eq. (2) in which $E_0{}^m$ is given by the ordinate *MM* in Fig. 1 and A_r is computed over the range of nuclear separation to the right of *TT*. The ordinate *PP* is drawn about equal to $A_r+E_0{}^m$, so that the LE appearance potential puts on the most probable electron energy the condition ${}^0E_e{}^m=PP-A_e$.*** The VC appearance potential puts a condition on the energy of the narrow band of high energy electrons, namely, that ${}^hE_e$ is approximately equal to an ordinate *SS* the position of which is not exactly defined;† and converting this to a condition on ${}^0E_e$ as was done in the case of the calibrating ion, we get for the span of the appearance-potential curve of the molecular ion,

$$\text{span}_2=J_1+H-A_e,$$

where $J_1=PP-SS$ in Fig. 1. Subtracting from this the span for the calibrating ion given in Eq. (4) we get

$$\text{span}_2-\text{span}_1=J_1-\frac{k_2\alpha}{k_1+k_2}. \tag{5}$$

Thus, assuming that the second term on the right side of Eq. (5) can be taken into account, examination of the feet of the appearance-potential curves in this case will yield a value for J_1, which indicates nothing more than a minimum value for the energy range over which the potential function of curve *II* is stable. A better value for the minimum energy range of stability would be obtained by the difference between the VC appearance potential *TT* for the atomic ion and the VC appearance potential *SS* for the molecular ion, providing, of course, that it could be established that the two types of ions originated in transitions involving the same potential function. It should be observed that even this closer approximation would not give the energy difference between the dissociation limit and the minimum of curve *II*; for the level L_2, constituting the upper level of the least energetic of the observable transitions, is not necessarily the lowest vibrational level of the upper state.

If we consider the production of atomic ions by transitions to curve *II* corresponding to internuclear distances lying to the left of *TT*, we arrive at an expression for the difference between the span for the atomic ion and the span for the calibrating ion identical with Eq. (5), except that J_2 appears in place of J_1. Thus, assuming again that the effects peculiar to the calibrating ion can be taken into account, examination of the feet of the appearance-potential curves with which we are at present concerned will give us a value for J_2, which is indicative of a minimum value for the slope of curve *II* in the Franck-Condon region. The value would be extremely rough without prior knowledge of the range of internuclear distances between *QQ* and *TT*. In the present case J_2 would also indicate the total energy released in dissociation following the transition to the level L_3 corresponding to the LE appearance potential; but the foot of an appearance-potential curve cannot be given this unique interpretation without prior

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[10] See curves *a*, *d*, and *f*, respectively, in Fig. 17 of Smyth's review article, Rev. Mod. Phys. **3**, 347 (1931).

*** From the definition of *PP* it is evident, by use of Eq. (3), that *PP* is also equal to the corrected LE appearance potential plus $k_2\alpha/k_1+k_2$.

† From the discussion of VC appearance potentials it is evident that the properly selected ordinate *SS* is equal to the corrected VC appearance potential.

knowledge of the relationships between the potential functions involved. For example, let us assume that the atomic ions produced by transitions to such a state as that represented by curve *III* are different from those just discussed, so that they can be distinguished in the mass spectrometer and their appearance-potential curve obtained. Examination of the foot of the curve as done in the other cases would yield a value for J_3. But this is only a fraction of the total energy released in dissociation following a transition to the level L_1' corresponding to the LE appearance potential; it is only an increment above that released in dissociation from the level L_2' corresponding to the VC appearance potential. It may, however, in distinction with the case just discussed, be rather closely indicative of the slope of the upper state potential function in the Franck-Condon region, providing that there is not considerable curvature in the function.

It is apparent that in the case in which the potential function of the upper state lies above the dissociation limit in the whole Franck-Condon region, as does curve *III*, the LE appearance potential of the fragment ion, properly corrected for the effect of the multiplicity of the lowest state of the calibrating ion, may give the transition energy in the center of the Franck-Condon region, uncertain to the extent of the effects of curvature of the upper state potential function and the effects of asymmetry in the expectation function of the ground level of the molecule, but independent of asymmetry in the electron energy distribution. However, for fragment ions produced by transitions to a state for which only part of the potential function lies above the dissociation limit, as illustrated by curve *II*, the LE appearance potential may correspond to a transition which is considerably removed from the center of the Franck-Condon region; and the range of curvature of the appearance-potential curve may not indicate even roughly the energy range of the upper state lying in the Franck-Condon region. Since it is generally unknown whether the upper state potential function is wholly or partly unstable in the Franck-Condon region, it seems clear, even within the limitations of the assumptions upon which the derivation of the significance of appearance potentials is based, that detailed examination of the foot of an appearance-potential curve is not likely to provide unambiguous information about the potential function of the ionic state involved. However, as the literature [2,10,11] shows, the magnitude of the appearance potentials themselves and other data obtainable by electron impact experiments can be helpful in testing proposals with regard to the nature of the potential functions of ionized states.

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[11] For predictions concerning the results of electron impact studies of H_2, for example, see: Condon and Smyth, Proc. Nat. Acad. Sci. **14**, 871 (1928); Condon, Phys. Rev. **35**, 658A (1930); and for experiments verifying the predictions, see: Bleakney and Tate, Phys. Rev. **35**, 658A (1930); Bleakney, Phys. Rev. **35**, 1180 (1930); **40**, 496 (1932); Lozier, Phys. Rev. **36**, 1285 and 1417 (1930); **44**, 575 (1933).