

## Theory of electron- $H_2^+$ dissociative collisions\*

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Two terms of the large-collision-energy expansion of the first Born cross section, the Bethe-Born (BB) cross section, are presented for ionization and for the total inelastic scattering in electron- $H_2^+$  collisions. An approximation made in an earlier calculation of the total inelastic BB cross section, which is known to produce an error in the second BB coefficient, is removed. Knowledge of these two theoretical cross sections makes possible a comparison of theory with the experimentally measured proton production, total dissociation, dissociative-excitation, and ionization cross sections for large collision energies. The theoretical dissociative-excitation cross section is calculated in the first Born approximation. Comparison between theory and experiment for all collision energies is accomplished by use of the Born dissociative-excitation cross section appropriately combined with the experimental ionization cross section. Experiment and theory agree within the expectations for first Born and BB theories. The measurements of the various cross sections from the different laboratories are shown to be mutually consistent.

### I. INTRODUCTION

The experimental study of electron-hydrogen molecule ion ( $H_2^+$ ) collisions has provided a comparatively mature picture of this system for collision energies greater than a few electron volts. Although the experimental techniques are sophisticated, the structure of  $H_2^+$  is well understood, and hence attractive to the theorist. The experimental measurements are also easily interpreted. The proton production cross section was measured first.<sup>1,2</sup> This cross section consists of  $\sigma(\text{ex}) + 2\sigma(I)$ , where

$$e^- + H_2^+(1s\sigma_g) \rightarrow H^+ + H^* + e^-, \quad \sigma(\text{ex})$$

and

$$e^- + H_2^+(1s\sigma_g) \rightarrow 2H^+ + 2e^-, \quad \sigma(I).$$

Here the  $H_2^+$  electronic ground state  $^2\Sigma_g^+$  is indicated by the  $1s\sigma_g$  orbital designation, and  $H^*$  stands for any bound hydrogenic state. Now experimental data are available for the dissociation cross section<sup>3,4</sup>  $\sigma(\text{ex}) + \sigma(I)$ , the dissociative-excitation cross section<sup>5</sup>  $\sigma(\text{ex})$ , and the ionization cross section<sup>6</sup>  $\sigma(I)$ . Most of the initial  $H_2^+(1s\sigma_g)$  vibrational-rotational states will be excited to repulsive parts of electronic potential energy curves if, as expected, the transitions obey the Franck-Condon principle. Some states near the  $H_2^+(1s\sigma_g)$  dissociation limit can be excited to bound vibration-rotation levels in certain final electronic states,<sup>7,8</sup> but the assumption that these events are rare has been accepted.<sup>1,2</sup> Direct vibrational excitation or dissociation of  $H_2^+$ , and various reactive processes, are also assumed to be unimportant. It follows that the dissociation cross sec-

tion can be equated to the total inelastic cross section.

The total inelastic cross section for molecular targets consists of a sum over every excited electronic state including the continuum, and over all rotational-vibrational states in each of the excited electronic states plus a sum over all rotational-vibrational excitations in the electronic ground state. As argued in the first paragraph, this last contribution can be ignored, at least for large collision energies. The remaining sum over the cross section has a strong analogy with the total inelastic cross section for an atomic target, which has only electronic degrees of freedom. Two terms in the asymptotic expansion of the Born cross section for large collision energies are introduced in order to take advantage of this situation. These two terms define the Bethe-Born (BB) cross section, which will be designated by the symbol  $Q$ . The advantages resulting from calculating the BB total inelastic cross section  $Q(T)$  in this manner have been well documented for the case of atomic targets; see Ref. 9 for a review. In addition, the obvious property that the BB dissociative-excitation cross section  $Q(\text{ex})$  automatically generates the BB ionization cross section  $Q(I)$ , once  $Q(T)$  is available, will be used.

The argument that inelastic events leading to discrete rotational-vibrational modes in excited electronic states are unlikely may be unique to  $H_2^+$ . In principle, only a "simple" correction term need be added to  $Q(T)$  if certain inelastic events are known not to contribute to the measured dissociation cross section. In practice, however, the added labor would be considerable (see Ref. 7 for an example of the type of calculation required),

and the importance of this property of  $H_2^+$  cannot be overemphasized.

The techniques used to construct the inelastic dipole-allowed BB cross section for atomic targets<sup>9</sup> are known not to apply to molecular targets.<sup>7,10</sup> Either of two approximations will reduce this molecular BB cross section to a form analogous to the atomic BB cross section, provided a sum over all rotational-vibrational states in the final electronic state is desired.<sup>7</sup> Either of the two additional approximations introduces a cross section for electronic excitation which depends on the internuclear separation. This approximate form will be used for both the Born and BB cross section; see Eqs. (2) and (5). The formal aspects of the molecular BB cross section used here are outlined in Sec. II. Section II also contains the definitions of other quantities pertinent to the remaining sections.

The BB cross section for ionization,  $Q(I)$ , can be calculated without evaluating discrete-continuum electronic matrix elements, but does require the Born matrix elements and expectation value between the ground state and all discrete electronic states. The considerable quantity of required data is summarized in Sec. III. A detailed presentation of Born matrix elements or, equivalently, generalized oscillator strengths, will not be given because of space limitations, although their publication is planned.<sup>11</sup>

Basic to this calculation of  $Q(I)$  is knowledge of the total inelastic BB cross section  $Q(T)$ . Although  $Q(T)$  has already been considered,<sup>12</sup> it is recalculated. This is presented because the earlier calculation is known to have an error in the second BB coefficient.<sup>12,13</sup> The error in the earlier calculation of the second BB coefficient is not small but, due to the relative unimportance of this quantity, it is argued that the improved coefficient will have very little effect on all but one of the published comparisons between experiment and theory.<sup>1-6</sup> The exception proves to be the comparison published for the ionization component.<sup>6</sup> The new data for  $Q(T)$  are also given in Sec. III.

The previous theoretical studies were done when there was a considerable uncertainty about the rotational-vibrational (RV) state distribution in the target  $H_2^+(1s\sigma_g)$ . Since many of the important inelastic processes are known to depend strongly on the initial RV state,<sup>14</sup> tabulations of theoretical data<sup>7,12,15</sup> were given for each of the RV states thought to be important. This problem has been, to a considerable extent, removed by the work of von Busch and Dunn.<sup>16</sup> They deduced a RV distribution consistent with their photodissociation cross section, which was measured for the identical  $H_2^+$  beam used in their electron-collision ex-

periment.<sup>1</sup> The von Busch-Dunn (vBD) distribution differs slightly from the Franck-Condon (FC) distribution which was assumed in the earlier comparisons<sup>1,2</sup> to best describe the  $H_2^+(1s\sigma_g)$  beam. Because of this development, the theoretical cross sections are given only for the vBD and FC averages. In the event that data are required for different RV averages, basic internuclear distance-dependent data are also presented.

The BB cross sections  $Q(T)$  and  $Q(I)$  are unusual in that their coefficients are not bounded by the corresponding coefficients for  $He^+(1s)$  and  $H(1s)$  targets. This result is somewhat unexpected,<sup>17,18</sup> since  $He^+(1s)$  and  $H(1s)$  represent the small and large internuclear-distance limits of the  $H_2^+(1s\sigma_g)$  target. The dominant factor in these coefficients is the dipole matrix element, and it is argued that the large contribution from this quantity for  $Q(T)$  and the unusually small dipole contribution to  $Q(I)$  are responsible for this surprise.

Theoretical data for  $Q(T)$  and  $Q(I)$  make it possible to construct a prediction for each of the measured dissociation cross sections. These comparisons are presented in Sec. IV, where it is argued that the agreement is good for large  $E$ , as it should be for BB theory. It is also concluded that the measurements from the different laboratories are consistent. Some discussion tending to question these conclusions has been voiced.<sup>19,20</sup> The resolution of the theoretical side, as pointed out in Ref. 20, depends on exactly how the various cross sections approach the BB behavior as  $E$  increases. To settle this point, the Born approximation to  $\sigma(\text{ex})$  is calculated from the data<sup>11</sup> used to generate  $Q(I)$ , for  $E < 1000$  eV. Predictions of the various dissociation cross sections are then constructed from the theoretically derived  $\sigma(\text{ex})$  and the *experimental* values<sup>6</sup> for  $\sigma(I)$ . These cross sections agree quite well with the corresponding experimental quantities over the entire range of  $E$ . This comparison also shows that the BB cross section has a remarkably variable range of applicability as a function of  $E$ . As anticipated by Dolder and Peart,<sup>20</sup> the BB form for  $\sigma(\text{ex}) + 2\sigma(I)$  and  $\sigma(I)$  is not clearly achieved for the largest collision energy for which measurements are available,  $E \sim 1000$  eV; the BB character for  $\sigma(\text{ex}) + \sigma(I)$  appears to be a reasonable approximation for  $E \sim 1000$  eV; and the BB form for  $\sigma(\text{ex})$  is accurate for  $E \geq 150$  eV.

Comparison of the present calculation of  $Q(I)$  with other calculations<sup>17,21,22</sup> is not given. Two of these calculations<sup>21,22</sup> are based on classical arguments and are not appropriate for the large- $E$  region. They have been compared with experiment elsewhere.<sup>6</sup> The remaining theoretical data<sup>17</sup> are based on first Born theory for ionization of  $He^+(1s)$

and  $\text{H}(1s)$  and an interpolation formula to generate the  $R$  dependence of the cross section. The substantial error in this procedure<sup>21</sup> is consistent with the unusual properties of  $Q(I)$  discussed in a preceding paragraph.

A short summary is presented in Sec. V. The general good agreement between experiment and theory is emphasized. However, the theoretical position is not without its shortcomings, and some of the more obvious improvements are anticipated.

## II. FORMALISM

The various forms of the first Born and BB cross sections used to treat electron-molecule scattering have been summarized elsewhere.<sup>18</sup> Hence, the following discussion will present the approximations and define quantities to be used in outline form, as the details can be found in the original papers.

The Born-Oppenheimer separation of electronic and nuclear motion is invariably used to describe the molecular target, so the initial  $\text{H}_2^+(1s\sigma_g)$  wave function  $\Psi$  can be written

$$\Psi(\vec{r}, \hat{R}) = \psi_o(\vec{r}, R) X_{\nu, J}(R) Y_{J, M}(\hat{R}). \quad (1)$$

The electronic eigenfunction  $\psi_o$  depends on the target electron position  $\vec{r} \equiv \vec{r}a_o$  referenced to the molecular frame, and on the magnitude of the internuclear separation  $R$ . The relative motion of the nuclei is described by  $X_{\nu, J}$ , where  $\nu$  is the number of radial nodes of  $X$ ; and by  $Y_{J, M}$ , where  $Y$  is a spherical harmonic,  $\hat{R}$  is a unit vector describing the orientation of the molecular frame with respect to some space-fixed axis, and  $J, M$  are the usual rotation quantum numbers.

The excitation of a molecular target from its initial state  $\psi_o$  to some final electronic state  $\psi_f$  is most often<sup>18</sup> treated by introducing an approximate Born cross section  $\sigma(O, f; R)$ , which depends only parametrically on internuclear separation, defined as

$$\frac{\sigma(O, f; R)}{\pi a_o^2} = 8 \left( \frac{v}{v_o} \right)^{-2} \int_{q_o(R)}^{q_1(R)} dq q^{-3} |\epsilon(O, f; q, R)|^2, \quad (2)$$

where

$$|\epsilon(O, f; q, R)|^2 \equiv (4\pi)^{-1} \int d\Omega(\hat{R}) \left| \int d\vec{r} \psi_f^*(e^{i\vec{q}\cdot\vec{r}} - Z_a e^{i\vec{q}\cdot\vec{r}_a} - Z_b e^{i\vec{q}\cdot\vec{r}_b}) \psi_o \right|^2. \quad (3)$$

Reference 18 gives a review of papers discussing the approximations, in addition to first Born theory, implied by Eq. (2), and the final form for this inelastic cross section; see Eq. (23).

Here  $v$  is the relative velocity of the target and projectile,  $v_o$  is the velocity of an electron in the first hydrogenic Bohr orbit, and  $a_o$  is the radius of this orbit. The quantity  $q$  is dimensionless, related to the momentum transfer by  $\hbar q/a_o$ , and its maximum and minimum values consistent with energy conservation are

$$q_{1,0}(R) = \mu v / m_e v_o \pm [(\mu v / m_e v_o)^2 - 2\mu \Delta E(O, f; R) / m_e H]^{1/2}. \quad (4)$$

The quantity  $m_e$  is the electron mass,  $\mu$  is the reduced mass of the collision partners,  $H$  is the Hartree unit of energy, and  $\Delta E(O, f; R)$  is the energy defect for the scattering event at the prevailing value of internuclear separation  $Ra_o$ . Equation (3) applies to a diatomic molecule, where  $Z_a, Z_b$  are the nuclear charges in units of the electron charge,  $\vec{r}_a, \vec{r}_b$  locate the nuclei in the space-fixed frame, and  $d\Omega$  is the element of solid angle for the unit vector  $\hat{R}$ .

The BB expansion for Eq. (2) is easily derived,<sup>23</sup> and it can be written in the form

$$Q(O, f; R) / \pi a_o^2 \equiv 8(v/v_o)^{-2} [M(O, f; R) \ln(v/v_o) + B(O, f; R) + L(O, f; R)], \quad (5)$$

where

$$M(O, f; R) \equiv \frac{1}{3} \left| \int d\vec{r} \psi_f^* \vec{r} \psi_o \right|^2, \quad (6)$$

$$L(O, f; R) \equiv -M(O, f; R) \ln[\Delta E(O, f; R) / H], \quad (7)$$

and

$$B(O, f; R) \equiv \int_0^1 dq q^{-3} [|\epsilon(O, f; q, R)|^2 - q^2 M(O, f; R)] + \int_1^\infty dq q^{-3} |\epsilon(O, f; q, R)|^2. \quad (8)$$

The convenience of the BB form will be exploited in the usual way<sup>9</sup> to construct the total inelastic cross section  $Q(T; R)$ , the ionization cross section  $Q(I; R)$ , and the excitation cross section  $Q(\text{ex}; R)$ . The relationship

$$Q(T; R) \equiv \left[ \sum_{f \neq 0} + \int \right] Q(O, f; R) = Q(\text{ex}; R) + Q(I; R) \quad (9)$$

is obvious when it is recognized that the first symbol enclosed by brackets signifies a sum over all discrete electronic states, and that the second in-

dicates an integral over the continuum electronic states. The closure relationship for the electronic eigenfunctions can be used with the result

$$Q(T; R)/\pi a_0^2 = 8(v/v_0)^{-2} [M(T, R) \ln(v/v_0) + L(T, R) + B(T, R)], \quad (10)$$

where

$$M(T, R) = \frac{1}{3} \left| \int d\vec{r} \psi_0^* |\vec{r}|^2 \psi_0 \right|^2, \quad (11)$$

$$L(T, R) = \left( \sum_f + \int \right) L(O, f; R) \equiv L(\text{ex}; R) + L(I; R), \quad (12)$$

and, for this one-electron target,

$$B(T, R) = \int_0^1 dq q^{-3} [1 - |\epsilon(O, O; q, R)|^2 - q^2 M(T, R)] + \int_1^\infty dq q^{-3} [1 - |\epsilon(O, O; q, R)|^2]. \quad (13)$$

The total inelastic cross section  $Q(T; R)$  could be calculated with only a knowledge of expectation values involving  $\psi_0$  if it were not for  $L(T, R)$ ; see Eqs. (10)–(13). Various schemes have been proposed for the estimation of  $L(T, R)$  when the complete set of matrix elements  $M(O, f; R)$  is not available. Rather than utilize any of these proposals, an adaptation of the moment-expansion

method will be used. This latter method was proposed, and shown to be useful for hydrogenic systems, by Green.<sup>24</sup>

As the technique is used here, a certain subset of the complete set of dipole matrix elements  $M(O, f; R)$  is assumed to be known. If the sum over the known matrix elements is designated by  $\sum_1$ , then the quantities

$$L(1; R) \equiv \sum_1 L(O, f; R),$$

$$M(1; R) \equiv \sum_1 M(O, f; R),$$

and

$$S(1; R) \equiv \sum_1 [\Delta E(O, f; R)/H] M(O, f; R)$$

are also known. The remainder of the closure sum over  $L$ , defined as  $\sum_2$  operating on  $L$  such that  $(\sum + f) = (\sum_1 + \sum_2)$ , is to be estimated by the moment method. By definition

$$L(T; R) = L(1; R) + \sum_2 L(O, f; R) = L(1; R) + L(2; R), \quad (14)$$

where  $L(2; R)$  is to be determined. The logarithmic term in  $L(O, f; R)$  [see Eq. (7)] is the quantity that prevents  $L(T; R)$  from having a simple closure expression, so this term is expanded in a Taylor series

$$\ln[\Delta E(O, f; R)/H] = \ln[\Delta E(2; R)/H] + [\Delta E(2; R)]^{-1} [\Delta E(O, f; R) - \Delta E(2; R)] + \dots \quad (15)$$

Equation (15) is substituted into the definition of  $L(2; R)$ . Only the first two terms of Eq. (15) are retained and  $\Delta E(2; R)$  is chosen to make the second term vanish. Then, using Eq. (7),

$$L(2; R) \cong -\ln[\Delta E(2; R)/H] \left( \sum_2 M(O, f; R) \right) \quad (16)$$

results where, by definition,

$$\Delta E(2; R) = \sum_2 \Delta E(O, f; R) M(O, f; R) / \sum_2 M(O, f; R). \quad (17)$$

The dipole-length and oscillator-strength sum rules allow Eqs. (16) and (17) to be rewritten as

$$L(2; R) \cong \ln[\Delta E(2; R)/H] [M(T; R) - M(1; R)] \quad (18)$$

and

$$\Delta E(2; R) = [\frac{1}{2}N - S(1; R)] / [M(T; R) - M(1; R)], \quad (19)$$

where  $N$  is the number of electrons in the target.

By hypothesis, all quantities appearing in Eqs. (18) and (19) are known and, consequently, approximate values for  $L(T; R)$  and  $L(2; R)$  are known. Equations (18) and (19) will be used to construct both the closure sum  $L(T; R)$  and its component corresponding to ionization  $L(I; R)$ .

The idea of a moment-expansion-like approximation has, of course, been used in many contexts, although it apparently has not been previously used for this particular problem. The success of Eqs. (14), (18), and (19) will depend upon keeping the unknown complement  $L(2; R)$  to a minimum.

Equations (10)–(14) complete the definition of  $Q(T; R)$ . The BB definition of  $Q(I; R)$  is also constructed to avoid the calculation of continuum matrix elements. An analog to Eq. (18) will be used to calculate  $L(I; R)$ . The remaining quantities required by  $Q(I; R)$  are

$$M(I; R) = M(T; R) - \sum_f M(O, f; R) \quad (20)$$

and

$$B(I; R) = B(T; R) - \sum_{f \neq 0} B(O, f; R), \quad (21)$$

where Eqs. (6) and (8) were used.

The  $\text{H}_2^+(1s\sigma_g)$  target is known to be in a broad range of vibrational-rotational states. If this distribution is given by  $(f_{vJ})$ , where  $\sum_{vJ} f_{vJ} = 1$ , it is convenient to introduce the "R distribution probability"

$$P(R) = R^2 \sum_{vJ} f_{vJ} |X_{vJ}(R)|^2. \quad (22)$$

Folding any of the  $R$ -dependent cross sections defined above with this function generates the corresponding total cross section. As a typical example,

$$\sigma(O, f) = \int dR P(R) \sigma(O, f; R) \quad (23)$$

defines the Born cross section for the electronic transition  $O \rightarrow f$  summed over all rotational-vibrational modes in the final electronic state  $f$  and averaged over all rotational-vibrational modes, as defined by Eq. (22), in the initial electronic state  $O$ .

The fact that the starting point of the above developments, Eq. (2), is an approximation to the first Born cross section for molecular scattering cannot be overemphasized. No specific information appears to be available on the expected difference between the correct first Born cross section and the approximate result based on Eqs. (2) and (23). Equations (2) and (23) are known to be consistent with the reflection approximation.<sup>18</sup> Hence, one can expect some of the analysis of this approximation to be applicable to the case under study. Problems can be constructed for which the reflection approximation predicts angular and/or energy distributions of dissociation fragments with large errors. However, even in these cases, the integrated cross section  $\sigma(O, f)$  [of Eq. (23)] can still be reasonably accurate, as Eq. (23) is based on a correct normalization procedure.

One of the main errors in the approximate  $\sigma(O, f)$  is probably associated with energy-conservation problems. This assertion has been proven<sup>10</sup> for the BB cross section  $Q(O, f)$ . The approximate  $Q(O, f)$  is defined by replacing  $\sigma(O, f; R)$  in Eq. (23) with  $Q(O, f; R)$  of Eq. (5), and by replacing  $\sigma(O, f)$  by  $Q(O, f)$ . The single error in the approximate  $Q(O, f; R)$  is in the quantity defined by Eq. (7), which contains the only remnant of the energy-conservation requirement left in the BB cross section.

Study of the correct BB cross section for a particular case has shown that the approximate form, Eqs. (5)–(8), can lead to both ambiguities and serious errors.<sup>7</sup> The largest errors were found when

both bound and dissociation modes of internuclear motion were possible in the final electronic state. However, even in this difficult case, the approximate cross section summed over all internuclear modes in the final electronic state,  $Q(O, f)$ , remained quite accurate.

It is fortunate, on the basis of the preceding discussion, that only cross sections analogous to Eq. (23) are required for comparison with experiment in this study. As more data differential in the dissociation energy and angle become available for comparison, theoretical data of the type defined by Eq. (2) will be required and, as a consequence, further analysis of the approximations may be necessary.

### III. NUMERICAL DATA

Numerical estimates of various  $R$ -dependent quantities are summarized in Table I. Rotational-vibrational averaged quantities, as implied by Eqs. (22) and (23), are given in Table II.

All matrix elements and expectation values discussed in this work are based on electronic eigenfunctions which were generated from known eigenparameters.<sup>25</sup> Numerical techniques used to evaluate powers of components of  $\vec{r}$  and many of the resulting numerical data used here are discussed in Ref. 26. Numerical values for the Born matrix element, Eq. (3), are based on the techniques discussed in Ref. 14, although some of the truncated expansions were extended beyond the limits used in Ref. 14.

The second column in Table I gives  $M(T, R)$  of Eq. (11), a quantity available from other sources.<sup>27</sup> Where comparisons are possible, agreement with previous work is acceptable, and any error in  $M(T, R)$  is presumed to be restricted to the last figure quoted.

The third and fourth columns list  $M(I; R)$ , which is defined by Eq. (20). As labeled, one column is known to be an upper bound. This follows from Eq. (20), the fact that the sum over discrete electronic states was truncated, and all  $M(O, f; R) \geq 0$ . The upper bound is based on the inclusion of the  $2-4p\sigma_u$ ,  $4, 5f\sigma_u$ ,  $6h\sigma_u$ ,  $2-6p\pi_u$ , and  $4f\pi_u$  orbitals in the sum appearing in Eq. (20). This corresponds to the inclusion of all states that correlate at large  $R$  to  $\text{H}^+$  and  $\text{H}$  with principal quantum number  $n \leq 3$ , plus some additional  $\pi_u$  states. The best estimate was obtained by using a quantum-defect argument to sum the contributions from the remaining  $np\pi_u$  orbitals. The exact value,  $M(T; 2.0) = 0.0362$ , which was obtained from the only published data for the  $1s\sigma_g$ -continuum dipole matrix elements,<sup>28</sup> is in reasonable agreement with the best estimate given in Table I. The error in the

TABLE I. Coefficients that define the  $R$ -dependent BB cross section [see the form of Eq. (10)] for the total inelastic cross section  $Q(T;R)$  and the ionization cross section  $Q(I,R)$ . Equations (11), (24), and (13) define  $M(T;R)$ ,  $L(T;R)$ , and  $B(T;R)$ , respectively, while Eqs. (20), (25), and (12) were used for  $M(I;R)$ ,  $L(I;R)$ , and  $B(I,R)$ , respectively.

$R$	$M(T;R)$	$M(I;R)^*$	$M(I;R)^a$	$L(T;R)$	$L(I;R)$	$B(T,R)$	$B(I,R)$
0	0.250 <sup>b</sup>		0.0708 <sup>c</sup>	-0.155 <sup>b</sup>	-0.074	0.2112 <sup>b</sup>	0.182 <sup>c</sup>
1	0.4558	0.0546	0.0499	-0.021	-0.031	0.2558	0.249
1.5	0.6141	0.0434	0.0381	0.156	-0.019	0.2596	0.288
2	0.7982	0.0414	0.0358	0.428	-0.015	0.2376	0.324
2.5	1.0103	0.0454	0.0396	0.821	-0.014	0.1846	0.355
3	1.2543	0.0543	0.0482	1.37	-0.012	0.0939	0.379
4	1.8579	0.0861	0.0798	3.14	-0.006	-0.2383	0.410
5	2.6426	0.1334	0.1271	6.24	0.010	-0.8437	0.424
6	3.618	0.180	0.173	11.3	0.031	-1.79	0.409
8	6.080	0.228	0.223	29.1	0.061	-4.79	0.400
10	9.161	0.255	0.251	60.4	0.078	-9.31	0.412
12	12.869	0.281	0.278	109	0.093		
$\infty$	$\infty$		0.2834 <sup>c</sup>	$\infty$	0.097 <sup>c</sup>	$-\infty$	0.532 <sup>c</sup>

\* Upper bound.

<sup>a</sup> Best estimate.

<sup>b</sup> These values were derived from data given in Ref. 32 and nuclear-charge scaling laws for hydrogenic matrix elements. For the hydrogen atom  $M(T)=1$ ,  $L(T)=0.7664$ , and  $B(T)=0.1515$ .

<sup>c</sup> These values were derived from data given in Ref. 33, nuclear-charge scaling laws for hydrogenic matrix elements, and the hydrogenic result  $L(I)=z^{-2}(0.0966-0.2834 \ln z^2)$  where  $z$  is the nuclear charge.

best estimate of  $M(T;R)$  is not known for other  $R$ , but hopefully it is confined to the last figure quoted. The largest errors will occur for large  $R$ , and are due to leaving out an estimate for the higher  $\sigma_u$  orbitals.

The use of the quantum-defect method for a molecule is somewhat open to question, since the principal quantum number is often different in the small- and large- $R$  limits. In general, the use of the united-atom principal quantum number seems most appropriate for finite  $R$  as long as the minimum  $n$  for which the estimate is to be used is shown to have the required  $n^{-3}$  behavior. The estimate for the  $n\rho\pi_u$  orbitals does not suffer from this ambiguity, as the  $n\rho\pi_u$  orbitals do not exhibit this change in  $n$  character for the limiting values of  $R$ .

The  $R$  dependence of  $M(I;R)$  shows a most un-

TABLE II. Coefficients  $A$  and  $C$ , which define the Bethe-Born cross section of Eqs. (26)–(29), for the indicated targets and rotational-vibrational averages defined by Eq. (22).

	$A(T)$	$C(T)$	$A(I)$	$C(I)$
He <sup>+</sup> (1s)	13.6	-29.4	3.86	1.7
H <sub>2</sub> <sup>+</sup> (1s $\sigma_g$ )FCP( $R$ )	61.7	-4.4	2.66	29.9
H <sub>2</sub> <sup>+</sup> (1s $\sigma_g$ )vBDP( $R$ )	59.2	-13.2	2.56	29.8
H(1s)	54.4	-42.1	15.4	28.2

usual property. It has a minimum at  $R=2.0$ , the  $R$  value for which the initial state shows maximum bonding. The reason for this is not known, but can be anticipated from the  $z$  component of  $M(T;R) - M(0, 2\rho\sigma_u; R)$ , which shows a similar minimum. Hence the sum of  $M(0, n\sigma_u; R)$  for  $n>2$ , including the continuum, must have a minimum at  $R\sim 2.0$ . In fact, the  $M(0, n\rho\sigma_u; R)$  for  $n>2$  have a zero in the neighborhood of  $R\sim 2.0$ , as has been observed for some members of this sequence.<sup>26,29</sup>

As discussed in Sec. II,  $L(T;R)$  and  $L(I;R)$  were calculated from Eqs. (18) and (19). In the  $L(T;R)$  case,  $\sum_i$  corresponds to the states listed above for the calculation of  $M(I;R)$ . The denominators of Eqs. (18) and (19) are just the upper bound to  $M(I;R)$  given in Table I, and the numerator of Eq. (19) is calculated from the same dipole data used for  $M(I;R)^*$ . The exact value for  $L(I;R)$  at  $R=2.0$  can be generated<sup>28</sup> and used to improve the estimate of  $L(T;R)$ . When this is done, a different value for  $L(T;R)$  is found. To ensure that the best value of  $L(T;R)$  is obtained,  $\Delta E(2;R)$  is replaced by  $\gamma\Delta E(1;R)$  and

$$L(T;R) \cong \sum_f^N L(O, f; R) - \ln\left(\frac{\gamma\Delta E(2;R)}{H}\right)[M(I;R)]^* \quad (24)$$

replaces Eq. (14). The value  $\gamma=0.926$ , which makes Eq. (24) exact for  $R=2.0$ , was used for all

$R$ . In the same way,

$$L(I, R) \cong -\ln[\xi \Delta E(2; R)/H][M(I; R)]^* \quad (25)$$

was used, where  $\xi = 0.929$  made Eq. (25) exact at  $R = 2.0$ . The numerator of Eq. (19) was estimated in the way used to calculate  $[M(I; R)]^*$ . The errors in these approximations to  $L(T; R)$  and  $L(I; R)$  should be small and confined to the last figure quoted for  $R \sim 2.0$ . The error in  $L(T; R)$  should not increase as  $R$  increases because of the dominance of the  $1s\sigma_g - 2p\sigma_u$  contribution; however, the error in  $L(I; R)$  is not known, and may become appreciable as  $R$  becomes large. Fortunately,  $L(I; R)$  is dominated by  $B(I, R)$ , as can be seen from the form of Eq. (10) and Table I, so the error of the  $O(v^{-2})$  term should not be excessive.

As an example of using Eqs. (14)–(19) to calculate  $L(T; R)$ ,  $L(1; 2.0) = 0.444$  and  $L(2; 2.0) = -0.019$  were found. According to Eq. (24), the correct value for  $L(2; 2.0)$  is  $-0.016$ . Equation (18) predicts  $L(I; 2.0) = -0.018$ , which is to be compared with the corrected value  $-0.015$  given in Table I. It is apparent from these numbers that  $L(2, R)$  is almost exclusively the ionization component of the closure sum, and that this component is small relative to  $L(T; R)$ . To reinforce the preceding discussion of  $R$  dependence,  $L(1; 5.0) = 6.23$  and  $L(2; 5.0) = 0.002$  were found, where the corrected value for  $L(2; 5.0)$  is  $0.01$ . The uncorrected ionization component is  $L(I; 5.0) = 0.001$ .

The calculation of  $B(T; R)$ , defined by Eq. (13), utilizes  $M(T; R)$  given in Table I and the Born expectation values for  $|\epsilon(O, O; q, R)|^2$  available elsewhere.<sup>11</sup> Equation (21) was used to estimate  $B(I; R)$ . The discrete state sum was truncated to include the set  $2-5s\sigma_g$ ,  $2-5p\sigma_u$ ,  $2-5p\pi_u$ ,  $3-5d\sigma_g$ ,  $4-5f\sigma_u$ ,  $5g\sigma_g$ ,  $6h\sigma_u$ ,  $4f\pi_u$ , and  $5g\pi_g$ . Estimates of the remaining discrete contributions from the  $ns\sigma_g$ ,  $np\sigma_u$ ,  $np\pi_u$ ,  $nd\pi_g$ ,  $nd\sigma_u$ , and  $nf\sigma_u$  orbitals with  $n > 5$  were obtained with the quantum-defect argument outlined above. The Born matrix elements  $|\epsilon(O, f; q, R)|^2$  used in this calculation are available elsewhere.<sup>11</sup> Any error in  $B(T; R)$  should be confined to the last figure quoted, while the error in  $B(I; R)$  is not known.

The quantity  $P(R)$  of Eq. (22) remains to be defined. Since the rotational states of the  $H_2^+(1s\sigma_g)$  target are expected to be reflected by small  $J$  values,<sup>16</sup> the approximation  $f_{\nu J} = f_{\nu 0} \delta_{J 0}$  will be used, where  $\delta_{J 0}$  is the Kronecker  $\delta$  function. Two sets of  $f_{\nu 0}$  will be used: one deduced from the Franck-Condon (FC) factors for the ionization of thermal  $H_2$  to form  $H_2^+(1s\sigma_g)$ <sup>30</sup> and the other (vBD), deduced from the experimental study of  $H_2^+(1s\sigma_g)$  photodissociation.<sup>16</sup> The vibrational eigenfunctions  $X_{\nu 0}(R)$  for  $0 \leq \nu \leq 19$  are the same as those used in a previous study of  $H_2^+(1s\sigma_g)$  scattering.<sup>7</sup> The two

constructions of  $P(R)$  are quite similar with the range  $1.5 \leq R \leq 3.5$  being most emphasized,<sup>31</sup> and with the FC  $P(R)$  tending to emphasize the larger  $R$  values somewhat more than the vBD  $P(R)$ .

The data given in Table I are sufficient for the calculation of  $Q(T; R)$  defined by Eq. (10), and of  $Q(I; R)$  which is defined by a similar equation. Substituting  $Q(T; R)$  and  $Q(I; R)$  for  $\sigma(O, f; R)$  appearing in Eq. (23) completes the definition of  $Q(T)$  and  $Q(I)$ . To facilitate the comparison of experiment with theory, the theoretical data will be given in the form

$$Q(T)/\pi a_0^2 = (E)^{-1}[A(T) \ln(E) + C(T)], \quad (26)$$

where

$$A(T) = 54.42 \int dR P(R) M(T; R), \quad (27)$$

and

$$C(T) = -2.61 A(T) + 108.84 \int dR \\ \times P(R)[L(T; R) + B(T; R)]. \quad (28)$$

Here  $E$  is the center-of-mass collision energy (in eV). The ionization cross section is defined by the obvious analogy with Eqs. (26)–(28). The resulting data are given in Table II, along with similar data for  $H(1s)$  and  $He^+(1s)$  targets.

The data given in Table II for  $A(T)$  and  $C(T)$  can be compared with a previous calculation of these quantities.<sup>12</sup> As claimed,  $A(T)$  from the previous calculation is correct, and is equal to the result quoted in Table II for the FC-averaged cross section. The earlier result for  $B(T)$  was based on an approximation designed to make  $A(T)$  correct, but was otherwise untested. The approximate value is  $C(T) \sim -42.8$  for the FC average.<sup>12</sup> This corresponds to an error of less than 15% in  $Q(T)$  for  $E = 100$  eV; the percentage error is, of course, less for larger  $E$ . This will have little effect on the comparisons of theory with experiment for  $\sigma(\text{ex}) + \sigma(I)$  or  $\sigma(\text{ex}) + 2\sigma(I)$  previously published,<sup>1-4, 16, 19</sup> but will change the comparison with  $\sigma(I)$  deduced<sup>6</sup> from the earlier calculation.<sup>12</sup>

The data in Table II are very interesting in that the molecular coefficients are not bound by the analogous quantities for the combined- and separated-atom limits of the molecular target. This was not expected,<sup>17, 18</sup> but can be anticipated from the data in Table I. The quantity  $M(T, R)$  increases like  $R^2$  as  $R$  becomes large because of the  $1s\sigma_g - 2p\sigma_u$  charge-transfer transition. In addition, this transition correlates to one normally included in the total inelastic cross section for the combined-atom limit. However, there is no analog to this charge-transfer transition in the separated-atom limit because these two molecular

states become degenerate in the separated-atom limit. It is not surprising then, that the molecular  $A(T)$  exceed the  $A(T)$  for the limiting- $R$  atomic targets. The minimum in  $M(I, R)$  was discussed above and, although it has not been proven, it may be that the unusual behavior in the  $z$  component of  $M(I, R)$  is also due to the presence of the charge-transfer transition.  $B(T)$  and  $B(I)$  are related to the values of the dipole matrix element in two ways [see Eqs. (12), (13), (27), and (28)]. These two relationships indicate that a decrease in  $M(I)$  will make  $B(I)$  more positive. Similarly, an increase in  $M(T)$  will make  $B(T)$  more negative. This is verified by the data presented in Table II. The extrapolation of these results to other molecular targets with allowed charge-transfer transitions may not be possible, but it does point out the dangers of guessing molecular parameters from knowledge of data for atomic systems to which the molecule correlates.

#### IV. COMPARISON WITH EXPERIMENT

Figure 1 shows the experimental<sup>6</sup>  $\sigma(I)$ , plotted in the manner that best exhibits the high-energy behavior of the cross section.<sup>9</sup> The theoretical data from Sec. III are shown as the solid line, and the estimate of  $Q(I)$  previously used to compare with experiment<sup>1-3, 6</sup> is indicated by the dashed curve.

The new results for  $Q(I)$  appear to predict the experimental slope of  $E\sigma(I)$  vs  $\ln E$ ,  $A(I)$ , reasonably well, provided that data for  $E < 500$  eV are ignored. The value of  $A(I)$  for the dashed line is necessarily too large, since only the  $2p\sigma_u$  and

$2p\pi_u$  states were used in Eq. (20) to define the  $M(I; R)$  that defines this  $A(I)$  through the analog to Eq. (27).

It is interesting that the old value of  $A(I)$  is probably closer to, but less than, the slope that one would predict by fitting the experimental data with the best straight line. Since the  $A(I)$  given in Table II is probably reasonably accurate, two points must be reemphasized. First, attempts to fit experimental data with the BB form should strongly emphasize the large- $E$  data, even though a "best" straight line may fit the data for a relatively large range of  $E$ . Second, the determination of the BB slope from experimental data is a very demanding exercise. This is because the cross section becomes smaller as  $E$  increases, and hence is harder to measure; and often the experimental limits on the cross section value increase with increasing  $E$  on the  $E\sigma$ -vs- $\log E$  plot.

The theoretical value of  $C(I)$  appears to be too large. This sign for any error in  $C(I)$  is reasonable, since the most prominent omissions from the discrete-state sum in Eq. (21) are the dipole forbidden  $nI\delta_{s,u}$  transitions. The neglect of such states will tend to make  $C(I)$  too large, as can be seen from Eqs. (8), (21), (25), and (28). Adjusting theory to experiment indicates that the theoretical  $C(I)$  could be as much as 20% too large. It is also just possible that the ionization cross section has not achieved its BB character for the largest  $E$  measurement, so that  $C(I)$  could be essentially correct.

The data presented here for  $Q(I)$  are the only high-energy theoretical data available in the BB form. One other Born calculation is available.<sup>17</sup>

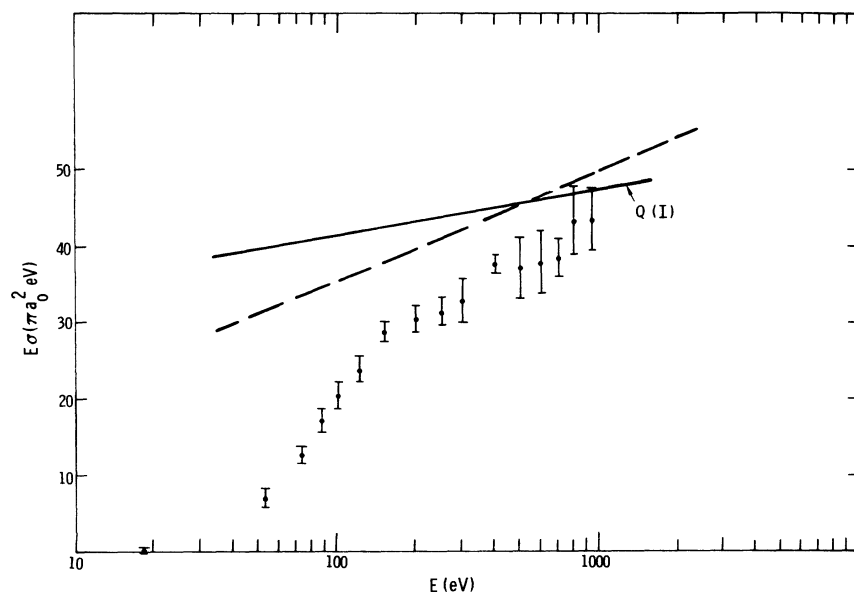


FIG. 1. Quantity  $E\sigma$  vs  $\log E$  for ionization electron- $H_2^+$  collisions. The solid curve is the BB cross section, Eq. (26), with the coefficients  $A(I)$  and  $C(I)$  given in Table II for the vBD rotational-vibrational average. The dashed curve is  $EQ/(\pi a_0^2 \text{ eV}) = 6.19 \ln(E/\text{eV}) + 6.97$  which is based on data from Ref. 12; see Eq. (9) of Ref. 1. The  $\bullet$  symbols represent the experimental data from Ref. 6.



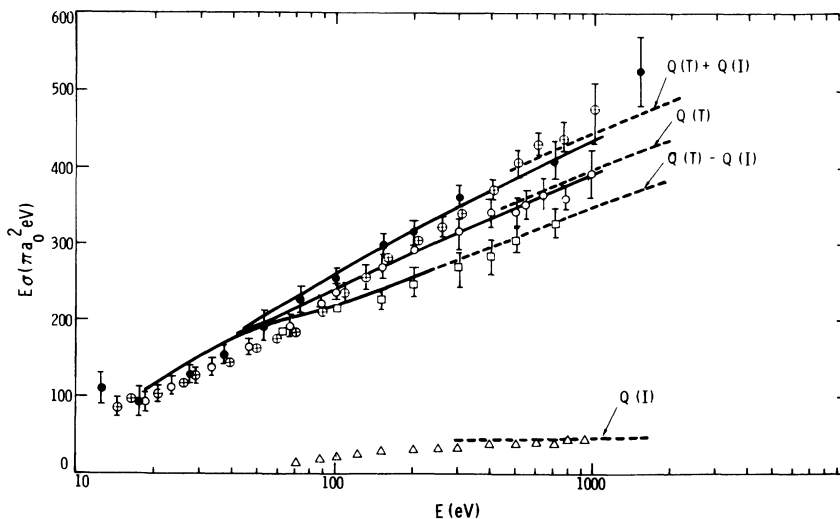


FIG. 2. Plot of  $E\sigma$  vs  $\log E$  for various dissociation cross sections for  $e^-$ - $\text{H}_2^+$  collisions. The dashed curves are BB data, Eq. (26), for the vBD-averaged coefficients given in Table II in the various indicated combinations. The solid curves are the first Born cross sections discussed in Sec. IV, corresponding to the various BB combinations approached for large  $E$ . The experimental data  $\bullet$ , Ref. 1, and  $\oplus$ , Ref. 2 are for  $\sigma(\text{ex}) + 2\sigma(I)$ ;  $\circ$ , Refs. 3 and 4, are for  $\sigma(\text{ex}) + \sigma(I)$ ;  $\square$ , Ref. 5, are for  $\sigma(\text{ex})$ ; and  $\triangle$ , Ref. 6, are for  $\sigma(I)$ . Experimental limits on the data points are schematically indicated for only a few of the data points for reasons of clarity.

This Born result was based on an  $R$  interpolation of the ionization cross sections for the combined- and separated-atom limits of this molecular target. Those data<sup>17</sup> are considerably too large,<sup>21</sup> an observation consistent with the discussion in Sec. III. Other theoretical ionization data<sup>21, 22</sup> are based on classical theories and predict  $A(I) = 0$ . Comparison of these data with experiment in the low- $E$  range, where these classical data are more acceptable, has been presented elsewhere.<sup>6</sup> Unfortunately, the  $R$  dependence of the classical theory was not investigated, so the effects of the rotational-vibrational distribution of the  $\text{H}_2^+$  target on the cross section could not be tested.

Now that the BB form for the ionization cross section  $Q(I)$  is known, the BB approximations to the proton-production cross section  $Q(T) + Q(I)$ , the total dissociation cross section  $Q(T)$ , and the dissociation-excitation cross section  $Q(T) - Q(I)$  can be compared with experiment. This comparison is presented in Fig. 2. In general, the agreement is good. The experimental data clearly separate into three groups for large  $E$ , and the predicted difference  $EQ(I)$  is reasonably consistent with the experimental difference for  $E = 1000$  eV.

The solid lines shown in Fig. 2 tending to merge with the various BB estimates were constructed in the following way. The  $1s\sigma_g - 2p\sigma_u$  cross section was taken from an unpublished manuscript<sup>31</sup> for small  $E$ , and from Ref. 7 for large  $E$ . The remaining contributions from discrete electronic

transitions were calculated with the generalized oscillator strengths discussed in Sec. III and with the theory discussed in Sec. II. These data are labeled  $\sigma(\Sigma^n)$  in Fig. 3. The ionization data required to complete this comparison were taken from the experimental measurement,<sup>6</sup> and the curve actually used is also shown in Fig. 3. These data are in good agreement with experiment for  $E > 100$  eV, and show some interesting features. The proton-production cross section  $\sigma(\text{ex}) + 2\sigma(I)$  approaches the BB cross section from below, as is usual,<sup>9</sup> but has not established BB behavior even for  $E = 1000$  eV. This reinforces the point, made here and elsewhere,<sup>20</sup> that the BB form may only apply for very large  $E$ . The total inelastic  $\sigma(\text{ex}) + \sigma(I)$  cross section shows similar behavior, except that it is essentially BB in character for  $E \approx 1000$  eV. The excitation cross section  $\sigma(\text{ex})$  approaches BB character from above, behavior apparently not previously observed,<sup>9</sup> and seems to be established for  $E \geq 150$  eV. The unusual behavior of  $\sigma(\text{ex})$  is undoubtedly due in part to the dominance of the  $1s\sigma_g - 2p\sigma_u$  transition and the  $\text{H}_2^+$  target's vibrational distribution function which emphasizes relatively large internuclear separations.

The data shown in Figs. 1 and 2 are based on the  $P(R)$  derived from the experimental distribution found by von Busch and Dunn.<sup>16</sup> The data derived from the FC  $P(R)$  cannot be ruled out on the basis of this comparison with experiment, but

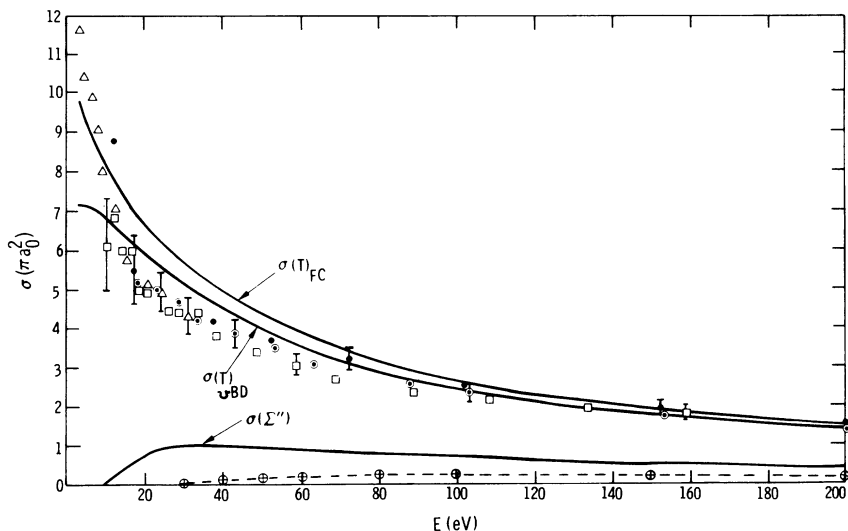


FIG. 3. Plot of  $\sigma$  vs  $E$  for various dissociative  $e^- - \text{H}_2^+$  collisions. The solid curves are first Born total inelastic cross sections discussed in Sec. IV;  $\sigma(T) = \sigma(2p\sigma_u) + \sigma(\Sigma'') + \sigma(I)$ . The experimental data  $\bullet$ , Ref. 1, and  $\square$ , Ref. 2, are for  $\sigma(\text{ex}) + 2\sigma(I)$ ;  $\circ$ , Ref. 3, and  $\triangle$ , Ref. 4, are for  $\sigma(\text{ex}) + \sigma(I)$ ; and  $\ominus$ , Ref. 6, represent  $\sigma(I)$ .

the theoretical data for the vBD distribution are in somewhat better agreement with experiment.

Figure 3 shows various experimental cross sections in the low- $E$  range. These cross sections differ only in the way in which  $\sigma(I)$  contributes to the measurement. Any difference in the experimental cross sections for  $\sigma(\text{ex}) + 2\sigma(I)$ ,  $\sigma(\text{ex}) + \sigma(I)$ , and  $\sigma(\text{ex})$  are difficult to detect because of the relative unimportance of  $\sigma(I)$  in this range of  $E$ . The theoretical data  $\sigma(\Sigma'')$  and  $\sigma(T)$  were discussed in a preceding paragraph.

Data derived from both the vBD and FC vibronic distributions are shown in Fig. 3, and they demonstrate the often stressed importance of this distribution. Obviously, it becomes more of a factor as  $E$  decreases, and it very likely accounts for some of the differences between experiments for small  $E$ .<sup>4</sup> The structure observed<sup>5</sup> in  $\sigma(\text{ex})$  for  $E \approx 100$  eV is not clearly reproduced by this calculation, and a better theory and/or mechanism not yet considered may be indicated. The agreement between experiment and theory for  $E < 200$  eV is better than expected, and probably should be considered fortuitous. This is unfortunate, since theory, if it were quantitative, could be used to investigate the target's rotational-vibrational population as was done in the photodissociation study of von Busch and Dunn.<sup>16</sup>

## V. DISCUSSION

The general good agreement between experiment and theory for the various dissociation cross sections in electron- $\text{H}_2^+$  collisions substantiates the following conclusions. The arguments<sup>20</sup> claiming consistency between the various experimental

measurements are reinforced. The thrust of this argument is that the BB behavior of experiment should not be presumed to apply at too low a collision energy. The various assumptions concerning the relationship between the measured and calculated quantities, as discussed in Sec. I, appear to be essentially correct. This conclusion, however, is tentative for the low- $E$  collisions, because of the danger of making quantitative claims for first Born theory in this energy range. One obvious problem is the dominant character of the higher vibrational states for small  $E$  and the possibility of exciting electronic states that do not dissociate.<sup>8</sup> Mechanisms not identified or considered, such as exchange or dissociative attachment, may also play important roles. Finally, serious questions about the approximations used to bring the molecular BB cross section into the form that applies to atomic targets, which are presented in Sec. II, are not demanded. Some reservations on this point are also advisable, since only limited experience is available; see the discussion in Sec. II.

The comparisons in Sec. IV indicate that the BB cross section may be of rather more limited utility than is sometimes assumed. The range of BB applicability varied from  $E \sim 100$  eV to  $E > 1000$  eV, depending on the process under study. This range is obviously inversely related to the "effective" energy defect of the relevant inelastic process. In addition, the approach of the first Born cross section to the BB cross section shows a quite different character than one might expect and, when possible, the full first Born cross section should be calculated.

The use of the first Born approximation for  $E$

less than a few hundred eV is itself the most compromising aspect of the theoretical data. The neglect of the Coulomb interaction of these electrically charged collision partners is clearly a problem,<sup>12</sup> and any number of additional shortcomings could be cited. It is clear, however, that it is necessary to accurately incorporate all aspects of this molecular target's structure in any improved theoretical treatment. A good example is provided here by the earlier<sup>12</sup> unexplored approximation to  $C(T)$  and the resulting effect on the comparison of theory with experiment for the ionization cross section.

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