Information-theoretic analysis of product rotational-state distributions using a perturbation method

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(Received 9 December 1985; revised manuscript received 10 October 1986)

Presently, quantal applications of atom—diatomic-molecule rearrangement collision processes to information-theoretic analysis have been limited to *ab initio* (exact close-coupling) methods. By taking into account symmetry consideration, a convenient expression for the analysis of rotational surprisal is deduced for the rearrangement collision process of $H + D_2 \rightarrow HD + D$. The dependency of rotational surprisal on collision energy and initial (reactant) rotational quantum state is examined. From a simple distorted-wave perturbation approach we find the propensity of near-linear surprisal at low collision energies and of deviation from linearity at higher collision energies.

I. INTRODUCTION

The application of information theory[1] to molecular collision dynamics (inelastic and reactive scattering) was initiated by Levine, Bernstein, Ben-Shaul, and Johnson about a decade ago.[2,3] Such application is useful for the codification, compaction, and correlation of experimental data on molecular collision dynamics.[3] Recently, quantal approaches[4,5] to study reactive scattering have been used for surprisal analysis based on the information-theoretic analysis. They are the exact close-coupling calculations of Wyatt[4] and of Kuppermann and Schatz[5] for the reactive scattering system of H_3.

Presently, there are largely two different quantal approaches to state-to-state reactive scattering: perturbation methods and exact close-coupling methods. Using the exact close-coupling methods, linear surprisal in the product rotational-state distributions of H_2 was demonstrated.[4,5] However, to date there exists no application of perturbation methods to such information-theoretical analysis. Here we apply the DWBA (distorted-wave Born approximation) method of Suck (Salk)[6-8] to the surprisal analysis of the product rotational state distributions of HD for $H + D_2 \rightarrow HD + D$.

II. DESCRIPTION OF THE ROTATIONAL SURPRISAL FOR $H + D_2 \rightarrow HD + D$

Considering symmetry for reactive transitions from the lowest para and orthostates of the reactant molecule (D_2) to the vibrational (n_b) and rotational (j_b) states of the product molecule HD for $H + D_2 \rightarrow HD + D$, we write the normalized final (product) rotational-state distributions

$$P_{j_b} = \tfrac{1}{3}[2\sigma(n_b, j_b \leftarrow n_a, j_a = 0) + \sigma(n_b, j_b \leftarrow n_a, j_a = 1)] , \quad (2.1)$$

where σ is the normalized state-to-state integrated cross section,

$$\sigma(n_b, j_b \leftarrow n_a, j_a) = \sigma_{\mathrm{DWBA}}(n_b, j_b \leftarrow n_a, j_a)/\sigma(n_b \mid n_a) ,$$

$$(2.2)$$

with

$$\sigma(n_b \mid n_a) = \frac{1}{3}\left[\sum_{j_b} 2\sigma_{\mathrm{DWBA}}(n_b, j_b \leftarrow n_a, j_a = 0) \right.$$

$$\left. + \sigma_{\mathrm{DWBA}}(n_b, j_b \leftarrow n_a, j_a = 1) \right] . \quad (2.3)$$

Here, $\sigma_{\mathrm{DWBA}}(n_b, j_b \leftarrow n_a, j_a)$ is the DWBA integrated cross section for a reactive transition from the reactant rovibrational state (n_a, j_a) to the product rovibrational state (n_b, j_b). n_a (n_b) denotes the vibrational quantum number of the reactant (product) molecule, and j_a (j_b) denotes the rotational quantum number of the reactant (product) molecule. For reactive transitions involving a single initial (reactant) rotational state j_a, we obtain

$$P_{j_b} = \sigma_{\mathrm{DWBA}}(n_b, j_b \leftarrow n_a, j_a) \Big/ \sum_{j_b} \sigma_{\mathrm{DWBA}}(n_b, j_b \leftarrow n_a, j_a) .$$

$$(2.4)$$

The prior expectation, i.e., guessed final-state distribution, is usually taken from the quantum-state counting of energetically available final (product) states; they are proportional to the number of translational states (density of states) and to the degeneracy of the final states available at a given total energy. The normalized prior expectation[3] is thus

$$P_{j_b}^0 = (2j_b + 1)E_t(n_b, j_b)^{1/2} \Big/ \sum_{j_b} (2j_b + 1)E_t(n_b, j_b)^{1/2} ,$$

$$(2.5)$$

where $E_t(n_b, j_b)$ is the translational energy (relative kinetic energy) in the final channel,

$$E_t(n_b, j_b) = E - E_{n_b} - E_{j_b} . \quad (2.6)$$

Here, E is the total energy, while E_{n_b} and E_{j_b} are, respectively, the vibrational and rotational energies corresponding to the final rovibrational state (n_b, j_b).

Following Levine and Bernstein[2] the information content, or entropy deficiency, ΔS of a distribution P_k is written

$$\Delta S = \sum_k I_k P_k , \tag{2.7}$$

where I_k is the surprisal for the kth product (final) state,

$$I_k = -\ln(P_k/P_k^0) . \tag{2.8}$$

Here, P_k and P_k^0 are, respectively, the true and guessed final-state distributions corresponding to the kth product state. The surprisal I_k measures the individual deviation of the actual outcome from the initial guess for the product molecular state k of interest. ΔS is then the measure of average deviation from the initial guess.

Now for the analysis of rotational surprisal we use the product rotational-state distribution P_{j_b} and the prior expectation $P_{j_b}^0$ to write

$$I_{j_b} = -\ln(P_{j_b}/P_{j_b}^0) . \tag{2.9}$$

The insertion of (2.1) and (2.5) into (2.9) leads to

$$\begin{aligned} I_{j_b} = &-\ln\tfrac{1}{3}[2\sigma(n_b,j_b \leftarrow n_a,j_a=0) \\ &+\sigma(n_b,j_b \leftarrow n_a,j_a=1)] \\ &+\ln(2j_b+1)E_t(n_b,j_b)^{1/2} \\ &-\ln\sum_{j_b}(2j_b+1)E_t(n_b,j_b)^{1/2} . \end{aligned} \tag{2.10}$$

The rotational surprisal is often plotted as a function of G_R,

$$G_R = E_{j_b}/(E - E_{n_b}) . \tag{2.11}$$

If linear rotational surprisal arises in some reactive collisions, we have the relation

$$I_{j_b} = \alpha G_R + \beta , \tag{2.12}$$

where α is the slope and β the intercept. Thus the product rotational-state distribution function becomes

$$P_{j_b} = P_{j_b}^0 e^{-\alpha G_R - \beta} . \tag{2.13}$$

Therefore, if a collision process favors the linear rotational surprisal, the virtue of the information-theoretic analysis here is that complete information on the product rotational-state distribution can be obtained by finding the coefficients α and β in (2.12) from the use of only a limited number (the minimum of two points) of integrated cross-section values.

III. COMPUTED RESULTS AND DISCUSSIONS

Calculations of the integrated cross sections σ_{DWBA} in (2.2) and (2.4) were made using the unperturbed molecular DWBA method of Suck (Salk).[6] The unperturbed molecular DWBA (Refs. 6, 8, and 9) does not introduce the effects of coupling. It represents the contribution of single-step reactive transition from the initial unperturbed state to the final unperturbed state, thus avoiding the effects of coupling. The effects of coupling are introduced in the CCBA (coupled-channel Born approximation) method[7,10] and exact close-coupling method.[11] Despite the neglect of coupling effects in the DWBA, it was previously shown[8]

that the predicted relative differential (but not absolute) and integrated cross sections agree well with the exact close-coupling results of Schatz and Kuppermann[11] and the product rotational-state distribution measurements of Marinero, Rettner, and Zare.[12] Earlier we reported the product rotational-state distributions for $H + D_2 \rightarrow HD + D$ only at a single collision energy of 1.3 eV. New to the present study is the examination of (1) the energy dependency of rotational surprisal, (2) the dependency of rotational surprisal on initial (reactant) rotational state, (3) the variation of rotational surprisal with product vibrational manifold at a given collision energy, and (4) differences between theories and measurements in the slope of linear rotational surprisals.

The potential surface employed for HD_2 is the analytic potential of Truhlar and Horowitz,[13] which was obtained from the *ab initio* Hartree-Fock potential surface of Liu and Siegbahn.[14] To avoid confusion with other DWBA methods, the unperturbed molecular DWBA of Suck (Salk)[6] is hereafter referred to as "S-DWBA."

Figure 1 shows a comparison of the S-DWBA with other theories for reactive transitions from the rovibrational ground state ($n_a=0, j_a=0$) of D_2 to the vibrational ($n_b=0$) ground-state manifold at the collision energy 0.55 eV. For simplicity we introduce the symbol V to represent the product vibrational manifold n_b in all the figures that appear in this paper. We find that the S-DWBA yielded general agreement with the CS (coupled-state) calculations of Schatz,[10] the SSDW (static-state distorted wave) results of Connor and Southall,[9] and the QCT (quasiclassical trajectory) study of Blais and Truhlar.[15] In particular, we find excellent agreement with the CS results of Schatz in the peak position of product rotational angular momentum at $j_b=2$ for $V=0$, and in the rotational-state distribution beyond this value. Earlier we[8] also found that at the higher collision energy of 1.3 eV the S-DWBA predicts normalized product (HD)
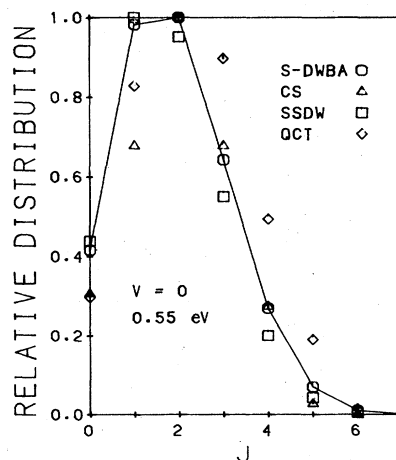

FIG. 1. Normalized product rotational-state distributions for $H + D_2(n_a=0, j_a=0) \rightarrow HD(n_b=0, j_b) + D$ at the collision energy of 0.55 eV. The line connects the points only for our DWBA results.
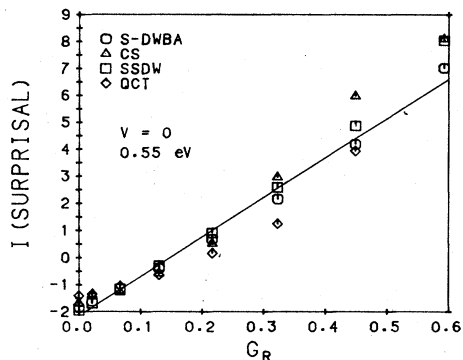
FIG. 2. Comparison of rotational surprisals between theories for the same state-to-state reactive transitions as in the case of Fig. 1. A straight line is shown only for our DWBA results.

FIG. 4. Comparison of rotational surprisals between theory and observation for reactive transitions to the product (HD) vibrational manifold of $V=2$ at the collision energy of 1.3 eV.

rotational-state distributions in good agreement with the experimental measurements of Marinero, Rattner, and Zare.[12] Figure 2 shows a comparison of rotational surprisals corresponding to the product rotational distributions shown in Fig. 1 at the collision energy of 0.55 eV. The S-DWBA (Ref. 6) predicted that rotational surprisal is nearly linear, in agreement with other theories.[9,10,15] Symbols shown in Figs. 1—12 are defined as follows: S-DWBA stands for our single-channel (unperturbed molecular) DWBA calculations;[6] CS, the coupled-state calculations of Schatz;[10] SSDW, the DWBA results of Connor and Southall;[9] QCT, the quasiclassical calculations of Blais and Truhlar;[15] and MRZ, the measurements of Marinero, Rettner, and Zare.[12] The rotational surprisals shown in Figs. 2—4 are our computed results from their product rotational-state distributions.[9,10,12,15]

In Figs. 3 and 4, using (2.10), we show the S-DWBA results (denoted by $\circ$) of symmetry-adapted linear suprisals for reactive transitions to the vibrational manifolds $n_b = 1$ and 2 including the MRZ measurement[12] and the SSDW calculation.[9] Common to both the perturbation results (S-DWBA and SSDW) and the measurements of Marinero, Rettner, and Zare is the general characteristics of linearity in the rotational surprisal. An observed
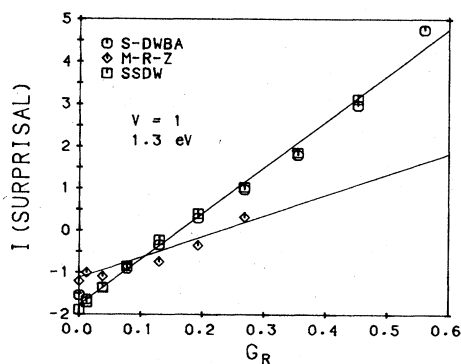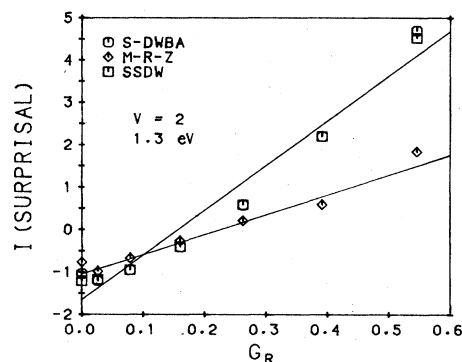
discrepancy in slope between the DWBA and the measurements is attributed to the difference in the width of the product rotational-state distributions. The SSDW results plotted in Figs. 3 and 4 are not symmetry adapted; that is, only the lowest para state ($j_a = 0$) contribution of the reactant molecule was taken into account. Later it will be shown from our S-DWBA calculations that the slopes of rotational surprisals between ortho and para states are nearly indistinguishable. Not shown in Figs. 3 and 4 are the measurements of Gerrity and Valentini[16] and the QCT results of Blais and Truhlar.[15] Their rotational surprisals showed lower slopes than the results displayed in Figs. 3 and 4, with some undulatory structures in rotational surprisals. In a rigorous sense, the measurements[12,16] mentioned above have not shown perfect linearity but general tendency of linearity.

Now using (2.4), separate rotational surprisals are calculated for reactive transitions from each of the rovibrational states, ($n_a = 0, j_a = 0$) and ($n_a = 0, j_a = 1$), of the reactant molecule D_2, to the vibrational manifolds $n_b = 0$, $n_b = 1$ and $n_b = 2$ of the product molecule HD. The results are shown in Figs. 5—10. We remind the reader that the symbol V which appears in Figs. 1—12 denotes the vi-

FIG. 3. Comparison of rotational surprisals between theory and observation for reactive transitions to the product (HD) vibrational manifold of $V=1$ at the collision energy of 1.3 eV.
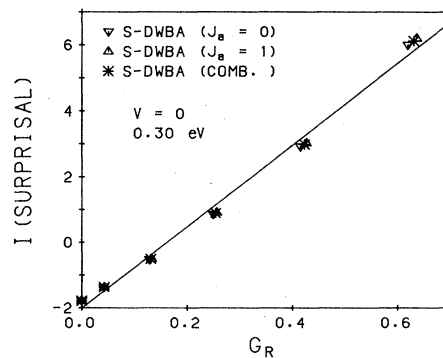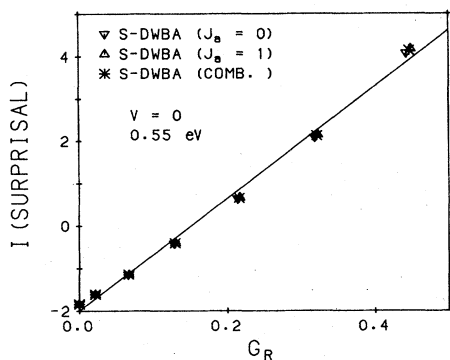

FIG. 5. Comparison of rotational surprisals between the para and ortho states of D_2 for reactive transition to $V=0$ at the collision energy of 0.3 eV; ∇ denotes the para state ($j_a = 0$) of D_2, $\triangle$ the ortho state ($j_a = 1$), and $*$ the combination of the two, that is, Eq. (2.10).
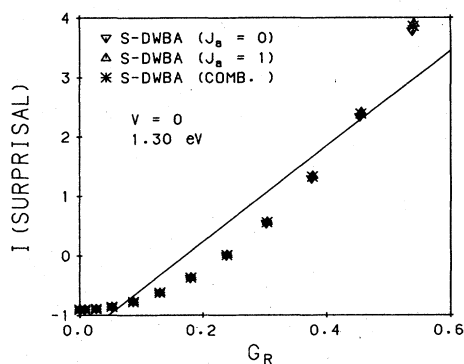
FIg. 6. Comparison of rotational surprisals between the para and ortho states of D_2 for reactive transition to $V=0$ at the collision energy of 0.55 eV; ∇ denotes the para state ($j_a=0$) of D_2, $\triangle$ the ortho state ($j_a=1$), and $*$ the combination of the two, that is, Eq. (2.10).

FIG. 8. Comparison of rotational surprisals between the para and ortho states of D_2 for reactive transition to $V=0$ at the collision energy of 1.3 eV; ∇ denotes the para state ($j_a=0$) of D_2, $\triangle$ the ortho state ($j_a=1$), and $*$ the combination of the two, that is, Eq. (2.10).

brational manifold n_b of the product molecule HD. It is interesting to note that for reactive transitions to all possible product vibrational manifolds ($V=0$, 1, and 2), near-linear surprisals with nearly identical slopes were observed for both of the initial rotational states $j_a=0$ and $j_a=1$ at the lower collision energies of 0.3, 0.55, and 0.9 eV. This implies that linear surprisals for reactive transitions which initiate from low-lying rotational states are generally in-

distinguishable in the structure of their relative product rotational-state distributions. The S-DWBA predicted linear surprisals contributed by the para state, $j_a=0$, are in close agreement with the SSDW of Connor and Southall,[9] who reported only the para state case for the product rotational-state distributions. For completeness, in Fig. 11 we show the ratios,

$$\sigma_{\text{DWBA}}(n_b=0, j_b\leftarrow n_a=0, j_a=1)/\sigma_{\text{DWBA}}(n_b=0, j_b\leftarrow n_a=0, j_a=0) ,$$

of symmetry-nonadapted cross sections at the peak position of rotational angular momentum (j_b) for product rotational distributions for reactive transitions to the $V=0$ vibrational manifold in order to assess the relative importance of the para- ($j_a=0$) and ortho- ($j_a=1$) state contributions. The peak positions were predicted to occur at the

product HD rotational angular momentum of $j_b=1$ at the collision energy $E_k=0.3$ eV, and at $j_b=2$ at both $E_k=0.55$ eV and $E_k=0.9$ eV, and $j_b=5$ at $E_k=1.3$ eV, showing the propensity of product molecule rotational excitation toward higher rotational angular momentum values with increasing collision energy. As shown in Fig.
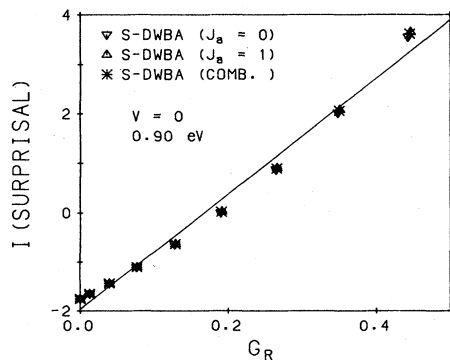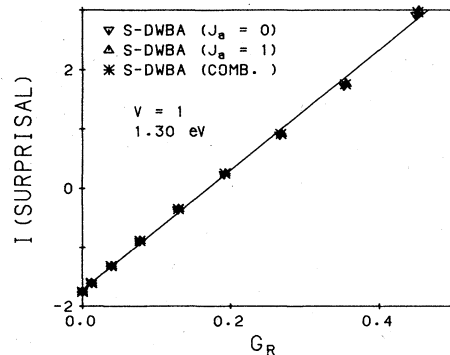

FIG. 7. Comparison of rotational surprisals between the para and ortho states of D_2 for reactive transition to $V=0$ at the collision energy of 0.9 eV; ∇ denotes the para state ($j_a=0$) of D_2, $\triangle$ the ortho state ($j_a=1$), and $*$ the combination of the two, that is, Eq. (2.10).

FIG. 9. Comparison of rotational surprisals between the para and ortho states of D_2 for reactive transition to $V=1$ at the collision energy of 1.3 eV; ∇ denotes the para state ($j_a=0$) of D_2, $\triangle$ the ortho state ($j_a=1$), and $*$ the combination of the two, that is, Eq. (2.10).
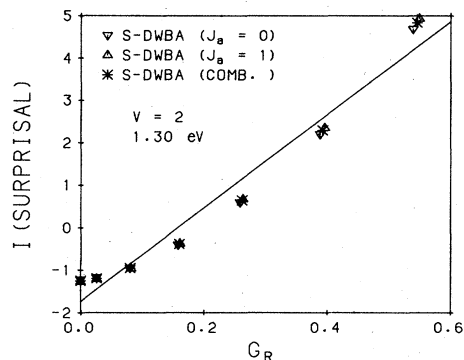
FIG. 10 Comparison of rotational surprisals between the para and ortho states of D_2 for reactive transition to $V=2$ at the collision energy of 1.3 eV; ∇ denotes the para state $(j_a=0)$ of D_2, $\triangle$ the ortho state $(j_a=1)$, and $*$ the combination of the two, that is, Eq. (2.10).

FIG. 12. Variation of surprisal slope as a function of collision energy for reactive transition to $V=0$.

11, we observed a gradual decrease in the ratio of cross section with collision energy. This suggests that as the collision energy increases the difference between the para- and ortho-state contributions to reactive transitions for the rearrangement collision of $H+D_2 \rightarrow HD+D$ is largely determined by spin symmetry (which, in turn, determines multiplicity).

As are shown in Figs. 2 and 5—7, we note that at all the lower collision energies of 0.3, 0.55, and 0.9 eV, rotational surprisals tend to be nearly linear. At the lower collision energies of 0.3 and 0.55 eV, reactive transitions to high product vibrational manifolds of $V=1$ and 2 are not energetically accessible. Among the collision energies we selected, the highest collision energy of 1.3 eV allows the
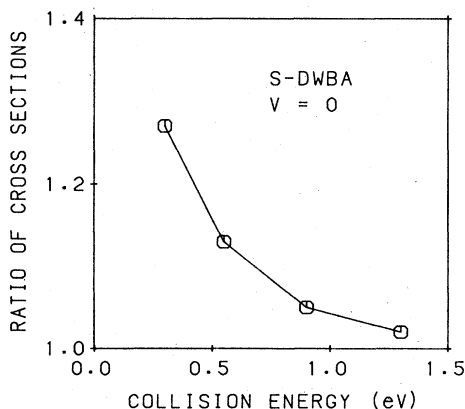
investigation of rotational surprisals involving the product vibrational manifolds of $V=0$, 1, and 2. They are shown in Figs. 8—10. We find that the structures of predicted rotational surprisals tend to deviate from linearity at this high collision energy as shown in Figs. 8 and 10. Finally, Fig. 12 plots the slope of rotational suprisals as a function of collision energy. The variation of the slope is seen to be nonlinear in collision energy, particularly for the reactive transitions to the $V=0$ product vibrational manifold.

IV. CONCLUSION

The following summary is in order: From the present information-theoretic analysis we have found that (1) the predicted rotational surprisals showed the general tendency of linearity at lower collision energies (as shown in Figs. 2 and 5—7) and of deviation from linearity at higher collision energies (as shown in Figs. 8 and 10), (2) reactive transitions (scattering) from the low-lying initial rotational states revealed indistinguishable slopes in the linear surprisals, indicating insensitivity to the small variation of rotational states in the reactant channel, and (3) there exists a nonlinear relationship between the variation of rotational surprisal slope and collision energy, as is shown in Fig. 12.

The deviation from linearity in rotational surprisal at a higher collision energy of 1.3 eV may be attributed to the failure of the DWBA as the contribution of inelastic channels becomes increasingly important with increasing collision energy. Thus it will be of great interest to see whether this conjecture is correct by using the CCBA methods,[7,10] which incorporate the contribution of such inelastic channels.

FIG. 11. Ration of cross sections, $\sigma_{DWBA}(n_b=0, j_b \leftarrow n_a=0, j_a=1)/\sigma_{DWBA}(n_b=0 j_b \leftarrow n_a=0 j_a=0)$, for $H+D_2 \rightarrow HD+D$ at the collision energies of 0.3, 0.55, 0.9, and 1.3 eV. j_b values are the peak positions of cross sections which occur at $j_b=1$ at $E_k=0.3$ eV, $j_b=2$ at $E_k=0.55$ and 0.9 eV, and $j_b=5$ at $E_k=1.3$ eV (see main text for further details).
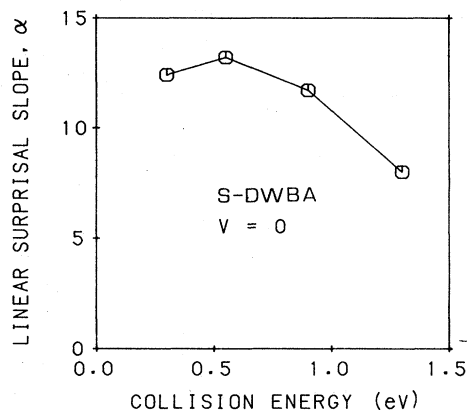
ACKNOWLEDGMENT

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