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Study of e-H_2 Scattering near the Rotational Threshold*

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Attention is called to the remarkable agreement between a recent experiment and the Gerjuoy-Stein theory based on the Born approximation for the rotational excitation of H_2 near threshold. The comparison is conducted through partial-wave analysis and application of the Wigner threshold law.

The recent experiment of Crompton *et al.*[1] measures the *absolute* e-H_2 cross section for the rotational transition $j=0$ to $j'=2$. Values of this cross section σ_{20} accurate to 5% are obtained for the incident energy of the electron from the rotational threshold at 0.0439 eV to the vibrational threshold at 0.52 eV. The purpose of this paper is to discuss the implications of this experiment for theory, in particular the Gerjuoy-Stein (GS) approach,[2] which is intended to be applicable in this low-energy range. Excellent agreement between theory and experiment is found from the threshold energy to ~0.07 eV, provided one replaces the GS value of the H_2 quadrupole moment with a more accurate one.[3] However, at higher energies, the theoretical results begin to fall short of the experimental ones; e.g., at 0.2 eV this discrepancy has increased to a factor of 2. To elucidate this situation, the GS cross section will be decomposed here into partial cross sections characterized by spherical incoming and outgoing waves, as is done in the adiabatic theory.[4] It is found that at threshold energies, the dominance of the $d \rightarrow s$ transition determines the threshold behavior of σ_{20} according to the Wigner law.[5] At the same time, the adiabatic theory proves inapplicable to this situation. However, at higher energies, this dominance passes on to a different $(p \rightarrow p)$ partial cross section and it becomes clear why the GS theory fails while the adiabatic theory applies.

To demonstrate these points, we begin by restating the essence of the GS theory.[2] This theory is based on three assumptions: (1) The Born approximation is valid; (2) only the quadrupole term in the expansion of the electron-molecule potential is significant; and (3) the large-r form of the quadrupole potential can be used throughout. Corrections to the rotational excitation cross section due to the above assumptions are, respectively, of the order (1) ka_0, (2) $(ka_0)^4$, and (3) $(ka_0)^2$, where k is the momentum transferred and a_0 is the Bohr radius. In the energy range of interest, $k \lesssim 0.1\ a_0^{-1}$, and extensive analysis[2] has demonstrated the smallness of these corrections.

For rotational excitation of the type $(j = j' \pm 2)$,

the GS cross section is given by

$$\sigma_{j'j} = \tfrac{16}{45}(k_f/k_i)Q^2\pi a_0^2(j200|j'0)^2, \quad (1)$$

where Q is the quadrupole moment of the molecule in a.u. (ea_0^2) and the last bracket is a Clebsch-Gordan coefficient. The initial and final wave numbers k_i and k_f are related by the conservation of energy:

$$k_i^2 + j(j+1)B = k_f^2 + j'(j'+1)B, \quad (2)$$

where B is the moment of inertia of the molecule. The threshold excitation energy of the $j=2$ state of hydrogen is $6B = 0.0439\,\text{eV}$.[6] For $k_i^2 \gtrsim 6B$, Eq. (1) can be written as

$$\sigma_{20} = \tfrac{16}{45}\, Q^2\kappa(\pi a_0^2)\ , \quad (3)$$

where κ is the final momentum in threshold units, i.e.,

$$\kappa = [(k_i^2 - 6B)/6B]^{1/2}\ .$$

In Fig. 1, the experimental data of Crompton *et al.*[1] are represented by points with error bars and plotted against κ. The points fall on a remarkably straight line. Furthermore, the value of $Q = 0.48 \pm 0.01$ deduced from the slope of this line is in excellent agreement with the theoretical value of 0.4857 calculated by Karl and Poll.[7] In fact, the solid line in Fig. 1 represents Eq. (3) with the theoretical value of Q, and it is seen to lie essentially within the error bars. It is suggested that further experiments of this type may be useful in determining the quadrupole moment of the target molecules.

Let us now expand the GS result by using a partial-wave analysis as is done for electron scattering from polar molecules.[8] Starting with Eq. (17) of GS, we have

$$\sigma_{j'j} = \frac{k_f}{k_i}\left(\frac{Qa_0}{2\pi^2}\right)^2 \left| \int d\vec{r}\, r^{-3} e^{i(\vec{k}_f - \vec{k}_i)\cdot\vec{r}} \int d\cos\Theta\, d\Phi \right.$$
$$\left. \times\, Y_f^* Y_i P_2(\vec{r}, \vec{s}) \right|^2 ; \quad (4)$$

the incoming and outgoing plane waves are expanded separately into partial waves. The resultant integrations over various angles can be readily performed, and the radial integral may be evaluated by a Bessel function integral.[9] The result is

$$\sigma_{j'j} = \tfrac{4}{5}(k_f/k_i)Q^2\pi a_0^2(j200|j'0)^2 \sum_{l_f} (2l_f+1) \sum_{l_i} |A|^2, \quad (5)$$

where

$$A = \left(\frac{k_f}{k_i}\right)^{l_f} \frac{2^{(l_i+l_f)/2}\left[\frac{1}{2}(l_i+l_f)-1\right]!}{(2l_f+1)!!(l_i-l_f+1)!!} (l_f 200|l_i 0) F$$
$$\times \left(\frac{l_f+l_i}{2}, \frac{l_f-l_i-1}{2}; l_f+\frac{3}{2}; \frac{k_f^2}{k_i^2}\right) ; \quad (6)$$

F is the hypergeometric function and the double factorial (!!) is the product of odd integers up to the argument. Note that in the limit $(k_f^2/k_i^2) \to 0$, $F \to 1$ and $\sigma_{j'j} \propto k_f^{2l_f+1}$, in agreement with the Wigner threshold law.[5] Indeed, in this limit Eq. (5) reduces to Eq. (1), with the contribution coming entirely from $l_f = 0$ and hence $l_i = 2$ as required by the Clebsch-Gordan coefficient in Eq. (6). The linearity of $\sigma_{j'j}$ as a function of k_f(or κ) emerges here as a direct consequence of the Wigner threshold law. In this energy region we have explicitly shown that the rotation of the molecule is predominantly excited by incoming d waves; the incident electron gives up two units of angular momentum directly to the molecule and departs as an s wave, as conjectured in an earlier paper.[10]

Hence to determine which region of r dominates the cross section at threshold, it suffices to examine only $\sigma(l_i = 2,\ l_f = 0)$. The relevant expression for the amplitude is

$$A \propto \int_0^\infty \frac{dr}{r} j_2(k_i r) j_0(k_f r). \quad (7)$$

Now when $k_f \simeq 0$, j_0 is $(1 - a/r)$, a being the scattering length, and j_2 is an oscillatory function. At very small values of r, j_2 has an r^2 dependence so the integrand is small provided that a is not large.[11] On the other hand, at very large values of r, contributions to the integral are also small because of the diminishing amplitudes of j_2, the weighting factor of r^{-1}, and the near cancellation of successive half-cycles of j_2. Therefore the dominant

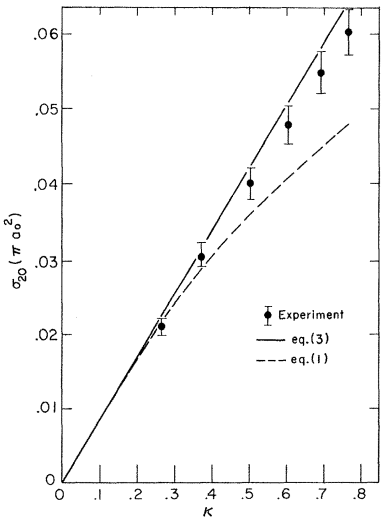

FIG. 1. Rotational cross section of H_2 σ_{20} plotted versus k_f in threshold units.

contribution to the integral in Eq. (6) comes from the vicinity of the first extremum of j_2, which occurs at $k_i r \simeq 3.3$, corresponding to $r \simeq 50\, a_0$. At this distance the potential $e\,QP_2(\cos\Theta)r^{-3}$ has fallen off to 10^{-4} eV even at $\Theta = 0°$, and is thus much smaller than the kinetic energy of the electron $\simeq 0.05$ eV. Therefore, it is not surprising that the Born approximation is valid. On the contrary, the basic assumption of the adiabatic theory is that the rotational energy, $6B = 0.044$ eV, is small compared with the electron's kinetic energy and the potential in the important region. We conclude that in the threshold region the adiabatic theory is not valid for the electron–neutral-molecule problem. However, if we were to consider the electron–molecular-ion problem, the Coulomb potential at a comparable distance would be much larger than the rotational energy. Therefore, the use of the adiabatic theory in the threshold region is well justified in the problems of e-H_2^+[10,12] and of photoionization of H_2.[13]

Returning to the problem at hand, we should mention that the agreement between theory and experiment shown in Fig. 1 is somewhat fortuitous. The actual GS result as given by Eq. (1) – rather than (3) – is shown by the dashed curve, which falls considerably short of the experimental data at the higher energies. It will be shown below that, as the incident energy increases, the cross section becomes increasingly dominated by the $(l_f = l_i = 1)$ rather than the $(l_f = 0, l_i = 2)$ contribution. Evidently the low-energy $^2\Sigma_u$ resonance[14] enhances the $(l_f = l_i = 1)$ contribution above the Born-approximation result, thus keeping the experimental points close to a straight line.

To verify the dominance of the $(l_f = l_i = 1)$ contribution in the GS theory as k_i^2 increases, consider the limit when k_f/k_i approaches 1. [Note that this limit is reached rather rapidly; e.g., even at $k_i^2 = 0.1$ eV, $k_f/k_i = 0.75$.] Equation (6) becomes then

$$A \to 4(l_f 200 \,|\, l_i 0)[(l_f + l_i)(l_f + l_i + 2)(3 - 2\delta_{l_f l_i})]^{-1}. \quad (8)$$

This result is identical to that of an adiabatic theory[4] if one evaluates phase shifts by the Born formula, using the large-r form of the quadrupole potential. Note that in this adiabatic Born approximation $\sigma(l_f = 0,\ l_i = 2)$ contributes to only 6% of the cross section, while $\sigma(l_f = l_i = 1)$ contributes 67%, and in fact the sum of all diagonal terms

$$\sum_{l_i=1}^{\infty} \sigma(l_i = l_f)$$

contributes 83%. It is evident that in the theory of GS, s-outgoing (and d-incoming) waves dominate the cross section near threshold, but quickly give way to pure p-waves as the energy increases.[15] However, the value of the p-wave partial cross section depends greatly on the occurrence of the broad $^2\Sigma_u$ resonance, whose existence has been predicted on grounds of the antibonding molecular orbital and confirmed experimentally.[14] This resonance cannot be evaluated by Born approximation and thus falls beyond the scope of the simple GS theory. Thus the discrepancies between GS theory and experiment by a factor of 2 at $k_i^2 = 0.2$ eV and 4 at $k_i^2 = 0.5$ eV are not surprising. Fortunately, at these energies, the adiabatic theory becomes valid. Alternatively, excellent results may be achieved by a close-coupling calculation.[16] (The appropriateness of the close-coupling and adiabatic approaches and their relationship are discussed elsewhere.[17]) Finally, the large contribution of diagonal terms to the cross section can be interpreted as approximate invariance of the electron's orbital angular momentum l in the collision process. This is a valuable concept in situations when the adiabatic theory is valid.[4,13]

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is given in Q. N. Watson, *Theory of Bessel Functions*, (Cambridge U. P., London, 1944), p. 401.

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Total Cross Section for Charge Transfer of Noble-Gas Ions N_2 †

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Absolute measurements are reported here of the total cross section σ_{10} for charge transfer of He^+, Ne^+, Ar^+, Kr^+, and Xe^+ in N_2 in the energy range from 10 to 100 keV. These measurements were obtained with ions produced in both an rf ion source and an electron-impact ion source. Differences are observed in the measured cross sections obtained with the different sources, except for Ne^+. These differences are attributed to metastable ions produced in the rf source. (Note: Ne^+ has no known metastable states.) The largest difference occurs with Xe^+ ions, where the ratio of the two measurements is 1.5 at a velocity of 2×10^7 cm/sec. In addition, a peak in the Xe^+ cross sections obtained with the rf ion source is not present in data taken with the electron-impact source. It is believed that the peak is caused by the near resonant charge transfer which can occur between metastable Xe^+ and dissociative ionization of N_2 or with excitation of N_2^+ to the $C^2\Sigma_u^+$ state.

I. INTRODUCTION

Radio-frequency ion sources have been utilized for many years to produce ions for use in charge-transfer and stripping cross-section measurements. Ion sources of this type are capable of imparting excessive energy to the gas being ionized, as evidenced by the extraction of doubly and triply ionized particles from the source. This is no problem when the source is used to produce H^+ ions. However, a problem does arise when an rf source is used to produce noble-gas ions and others with metastable states. All noble-gas ions except Ne^+ have known metastable states. There are one in He^+ and four each in Ar^+, Kr^+, and Xe^+. Thus, cross sections obtained with these ions can be influenced by the presence of metastable ions in the incident beam. To further complicate the situation, there is no established method at present to determine how many of the ions are in a given metastable state for ions of the energy range used here. The number in a given metastable state will most likely depend on source-operating parameters. Thus, cross sections measured with these ions cannot be realistically compared with theory or data of other investigators.

To determine the extent of the cross-section dependence on the presence of metastable ions in a beam from an rf ion source, the total cross section for charge-transfer σ_{10} was measured with the use of both an rf source and an electron-impact (EI) source. The EI source was operated in such a manner that the electron energy was sufficient to singly ionize the gas but not sufficient to excite it to any of its metastable states in a single collision. For all ions which have metastable states, the cross sections obtained with the two sources differed. It is important to note that the measured differences are meaningful only for the particular rf source and its operating parameters. However, the differences are indicative of what can be expected when an attempt is made to compare data obtained with any rf source.

The total cross sections measured with the EI source constitute a reliable set of data on the charge transfer of an electron from room-temperature N_2 to ground-state noble-gas ions.

Section II describes the apparatus and procedures used in obtaining the data. In Sec. III the data are presented. Results are discussed in Sec. IV.

II. APPARATUS AND PROCEDURE

The Sandia Laboratories 100-kV ion accelerator was used in this study. The accelerator delivers a beam of magnetically analyzed ions having small energy spread to the experimental chamber. The energy is measured to 2%. As stated in the