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PENNING IONIZATION OF H<sub>2</sub> BY He(23S): QUANTUM MECHANICAL SCATTERING CALCULATIONS WITHIN THE RIGID-ROTOR APPROXIMATION

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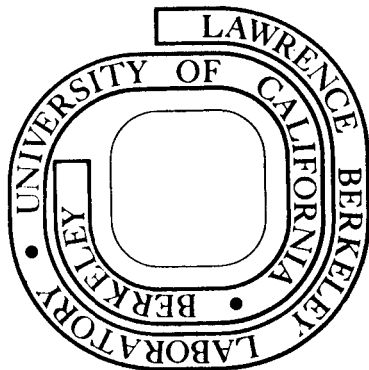
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Penning Ionization of  $H_2$  by  $He(2^3S)$ : Quantum Mechanical  
Scattering Calculations within the Rigid-Rotor Approximation\*

Albert P. Hickman, Alan D. Isaacson, and William H. Miller<sup>†</sup>

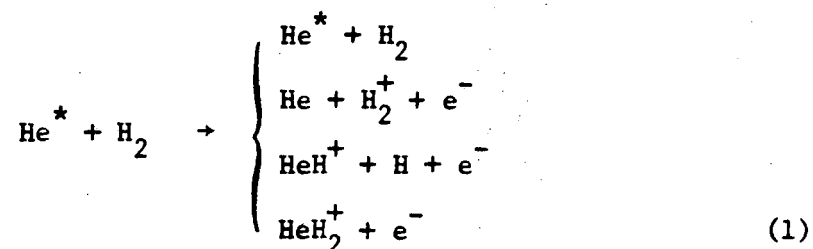
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Abstract

Elastic, rotationally inelastic, and total ionization cross sections have been calculated quantum mechanically for the scattering of metastable  $He(2^3S)$  atoms by  $H_2$  in the energy range 0.010 to 0.500 eV. The potential surface  $V^*$  and autoionization width  $\Gamma$  previously calculated by the authors were used. The scattering calculation was based on the Arthurs and Dalgarno formalism for the scattering of an atom by a rigid rotator. The coupled channel equations were solved numerically for the complex, angularly dependent potential  $V^* - \frac{i}{2} \Gamma$ . The results show that the total ionization cross section  $\sigma_i$  increases sharply with energy. Hence the ionization rate constant has a strong temperature dependence. The calculated rate constants are in good agreement with the experimental results of Lindinger, et al.

## I. Introduction

The scattering of  $H_2$  and the triplet metastable state of helium [ $He(2^3S)$ ] is the prototype of "chemiionization" because several elastic and reactive channels are possible:



This process is ideal for theoretical study for several reasons. First, rather extensive CI calculations are feasible because the system has few electrons. We have already reported<sup>1</sup> the potential surfaces  $V^*$ ,  $V_+$ , and  $\Gamma$  necessary to treat these reactions. ( $V^*$  and  $V_+$  are Born-Oppenheimer potential surfaces for  $He^*H_2$  and  $HeH_2^+$ , respectively and  $\Gamma/h$  is the probability of molecular autoionization per unit time as a function of the nuclear coordinates.) Second, the interaction  $V^*$  between  $He^*$  and  $H_2$  is predominantly repulsive, so the various possible reactions should be strongly energy dependent. Hence the accuracy of the calculated cross sections provides a sensitive test of the potentials. Thirdly, considerable experimental data on this system<sup>2-6</sup> are available for comparison.

Preston and Cohen<sup>7</sup> have treated this system using a classical trajectory model and obtained cross sections for ionization into the various possible final channels. In the present work, we report quantum mechanical calculations of elastic, rotationally inelastic, and total ionization cross sections. The treatment is exact within the framework of the Arthurs and Dalgarno<sup>8</sup>

formalism for the scattering of an atom by a rigid rotator. (A direct comparison between the classical and quantum mechanical calculations is presently not possible, because different potential surfaces and widths were used.) In Section II we discuss the modifications in the scattering formalism necessary when a complex potential  $V^* - \frac{1}{2}\Gamma$  is used to describe Penning ionization. Section III contains our results and discussion, and Section IV is a summary.

## II. Theory

The Arthurs-Dalgarno<sup>8</sup> formalism for the scattering of an atom by a rigid rotator is well known. In the present application, however, we describe the loss of incident He\* atoms due to Penning ionization by using a complex potential,<sup>9-12</sup>  $V^* - \frac{1}{2} \Gamma$ . We will discuss here only the changes which result from the addition of an imaginary part to the potential.

(1) The coupled-channel equations have complex solutions. These solutions were generated using the Numerov algorithm,<sup>13</sup> generalized to complex arithmetic. By separating the real and imaginary parts of all equations, N coupled complex equations may be replaced by 2N coupled real equations, to which N linearly independent solutions must be found.

(2) The customary R-matrix boundary conditions<sup>13</sup> were not applied. Normally, real solutions lead to a real R-matrix, from which the S-matrix is easily generated. In the present case it was simpler to match the asymptotic form of the complex solutions directly to a complex S-matrix. We shall briefly indicate how this was done. Following the notation of Arthurs and Dalgarno,<sup>8</sup> we write the desired asymptotic solutions as

$$\begin{aligned}
 U_{j'l'}^J(R) \sim & \delta_{jj'} \delta_{ll'} \exp[-i(k_j R - l\pi/2)] \\
 & - (k_j/k_{j'})^{1/2} S^J(j'l', j'l) \exp[i(k_{j'} R - l'\pi/2)] \quad . \quad (2)
 \end{aligned}$$

For each J, this may be rewritten in terms of N x N complex matrices:

$$\underline{U}^J = \underline{H}^- - \underline{H}^+ \underline{K}^{-1/2} \underline{S}^J \underline{K}^{1/2} \quad (3)$$

where the elements of  $\underline{U}^J$  are  $U_{j'l'}^{J,jl}$  and

$$H_{j'l',jl}^{\pm} = \delta_{jj'} \delta_{ll'} k_{jR} [n_{\ell}(k_{jR}) \pm i j_{\ell}(k_{jR})] \quad (4)$$

and

$$K_{j'l',jl} = \delta_{jj'} \delta_{ll'} k_j \quad (5)$$

$j_{\ell}$  and  $n_{\ell}$  are spherical Bessel functions. The  $N$  linearly independent solutions actually generated from the coupled equations may be written as an  $N \times N$  complex matrix  $\underline{Y}^J$ . Asymptotic boundary matching to satisfy conditions (3) is accomplished by solving

$$\underline{H}_1^- \underline{A} + \underline{H}_1^+ \underline{B} = \underline{Y}_1^J \quad (6)$$

$$\underline{H}_2^- \underline{A} + \underline{H}_2^+ \underline{B} = \underline{Y}_2^J \quad (7)$$

where the subscripts indicate the matrices evaluated at asymptotic values  $R_1$  and  $R_2$ . Then

$$\underline{S}^J = - \underline{K}^{1/2} \underline{B} \underline{A}^{-1} \underline{K}^{-1/2} \quad (8)$$

For the actual computation, it was found convenient to separate the real and imaginary parts of all of the above equations.

(3) Ionization cross sections must be defined. If the rotator is initially in the  $j^{\text{th}}$  rotational state, and the initial translational kinetic energy is  $k_j$ , then the total ionization cross section is

$$\sigma_{\text{ion}}(j) = \frac{\pi}{(2j+1)k_j^2} \sum_{J=0}^{\infty} \sum_{\ell=|J-j|}^{J+j} (2J+1) \left\{ 1 - \sum_{j'l'} |S^J(j'l',jl)|^2 \right\} \quad (9)$$



This formula is derived by inverting the normal proof<sup>14</sup> that the S matrix is unitary, which is based on the assumption of flux conservation. The lack of unitarity causes the term in braces to be nonzero and hence describes the loss of flux. It should be noted that  $\sigma_{ion}(j)$  is the sum over all possible final ionization channels. The present formalism yields no information about the relative population of final channels. All other cross sections for elastic scattering and rotational excitation are written in terms of the S matrix elements as described by Arthurs and Dalgarno.<sup>8</sup>

### III. Results and Discussion

We have calculated elastic, rotationally inelastic, and total ionization cross sections at several energies between 0.010 and 0.500 eV. Rate constants for ionization were determined for  $T = 300$  to  $900^\circ\text{K}$  by taking thermal averages. In this section we will mention certain details of the scattering calculation, and then discuss the results obtained.

The potential  $V^* - \frac{1}{2} \Gamma$  was calculated in the previous paper for several values of  $R$ ,  $\theta$ , and  $r$ . These coordinates are illustrated in Figure 1. If one freezes the  $\text{H}_2$  bond distance at its equilibrium value ( $r = 1.4 a_0$ ), then the potential may be expanded as a sum of even order Legendre polynomials:

$$V^* - \frac{1}{2} \Gamma = \sum_{\ell} (v_{\ell}(R) - \frac{1}{2} \Gamma_{\ell}(R)) P_{\ell}(\cos\theta) \quad (10)$$

In the previous paper, we found that this series was very quickly convergent. Table 1 lists the values computed for  $v_0$ ,  $v_2$ ,  $v_4$ ,  $\Gamma_0$ , and  $\Gamma_2$ . For our calculations we used cubic spline interpolations for  $v_0$ ,  $v_2$ , and  $\Gamma_0$ .  $v_0$  was set to zero for  $R \geq 11 a_0$ ; for  $R \geq 9 a_0$   $v_2$  was set to zero, and  $\Gamma_0$  was given the asymptotic form  $(14.008) \exp(-2.0177 R) \text{ au}$ , which fits exactly the calculated values at  $R = 9 a_0$  and  $10 a_0$ . For all  $R$ ,  $\Gamma_2$  was fit by the expression  $(0.73648) \exp(-1.7924 R) \text{ au}$ , and  $v_4$  was fit by  $(0.08375) \exp(-1.2015 R) \text{ au}$ . In the energy range 0.010 to 0.500 eV, the ionization cross sections were quite insensitive to whether or not  $\Gamma_2$  and  $v_4$  were included.  $v_4$  had a minor effect on the rotational excitation cross sections, which will be discussed below.

Only open channels were included in the calculation, and various tests indicate that this was sufficient. Just above the threshold for rotational excitation from  $j = 0$  to  $j = 2$ , including the just-opened channel made less than 2% contribution to the ionization cross section. A similar test just above the  $j = 0$  to  $j = 4$  threshold gave the same result. In this case, however, the cross section for  $j = 0$  to  $j = 2$  rotational excitation increased about 12% (for small partial waves) when the  $j = 4$  channel was added. Tests at higher energies confirmed that including only the  $j = 0$  and  $j = 2$  rotational states was sufficient to obtain converged ionization cross sections. The rotational excitation cross sections were more sensitive to the addition of extra channels.

The ionization cross sections as a function of energy are tabulated in Table 2. We have assumed that the target  $H_2$  is initially in the  $j = 0$  rotational state. Trial calculations were performed assuming initial rotational states of  $j = 1$  and  $j = 2$ . For an initial (center of mass) translational energy  $E = 0.100$  eV, the ionization cross sections decreased 1% and 3% when the initial rotational state was  $j = 1$  and  $j = 2$ , respectively. For  $E = 200$  meV, the corresponding changes were 4% and 10%.

The most striking feature of the cross sections in Table 2 is the strong energy dependence. This reflects the interplay between the repulsive potential  $V^*$  and the exponential form of  $\Gamma$ . Generally speaking, at higher energies the collision partners approach each other more closely, and "see" larger values of  $\Gamma$ .

Table 3 gives rotational excitation cross sections ( $j=0$  to  $j=2$ ) as a function of energy. Like  $\sigma_1$ ,  $\sigma_{0 \rightarrow 2}$  also increases sharply with collision

energy, and a similar physical explanation can be given. Since  $v_0 > v_2$ , the interaction is predominantly spherically symmetric, and only close collisions probe  $v_2$ . Since the torque necessary for rotational excitation can be transmitted only through  $v_2$  (and higher order terms),  $\sigma_{0 \rightarrow 2}$  depends critically on the amount of  $v_2$  "seen" on a trajectory. Like  $\Gamma$ ,  $v_2$  increases exponentially with decreasing  $R$ , so the energy dependence of  $\sigma_{0 \rightarrow 2}$  is similar to that of  $\sigma_1$ . An important mathematical distinction should be made, however. The coupled-channel equations describe a probability flux in and out of the various rotational channels, which are coupled by  $v_2$ . Penning ionization, however, as modelled by adding an imaginary part to the potential, is a probability "sink". Once flux is lost to the ionization channel it cannot be recovered.

We have also calculated the angular distribution of  $\text{He}(2^3\text{S})$  in elastic collisions at 0.100 eV, assuming the initial and final rotational states of  $\text{H}_2$  are  $j = 0$ . Two important conclusions may be drawn from our results. First, the Penning ionization channel causes a decrease mainly in the large-angle elastic scattering. Figure 2 compares  $\frac{d\sigma}{d\theta}$  calculated using both  $V^*$  alone and  $V^* - \frac{1}{2}\Gamma$ , to show the effect of "turning on" the ionization channel. These results are consistent with the picture that small impact parameter collisions lead to ionization, because (with  $V^*$  repulsive) such collisions also lead to large scattering angles. The second conclusion of our calculation is that the differential elastic cross sections ( $\frac{d\sigma}{d\theta}$ ) are quite insensitive to  $v_2$  and  $\Gamma_2$ . Neither curve in Figure 2 changed noticeably when the nonspherical terms of the potential and width were omitted. The largest change (5%) was at  $180^\circ$ . For smaller angles ( $\theta \leq 90^\circ$ ) there was

essentially no change at all. It should not be concluded, however, that  $v_2$  can be neglected entirely, since it did have a more pronounced effect ( $\sim 10\%$  at 0.100 eV) on the total ionization cross section.

Figure 3 shows the comparison between our calculation and experiment. Rate constants are obtained by taking the appropriate thermal average of  $\sigma_1(E)$ , assuming a Maxwellian distribution of collision energies  $E$ . The results agree reasonably well with the data of Lindinger et al.,<sup>15</sup> whose experimental error was  $\pm 30\%$ . The strong temperature dependence is correctly reproduced, but the numerical values seem to be slightly small. Any of several factors could explain this small discrepancy.  $\Gamma$  may be too small, as the calculation of the width was based on an approximation to the correct background continuum function. Alternatively, the real part of the potential surface may be too repulsive. The cross sections would be strongly affected by such an error in  $V^*$ , due to the exponential form of  $\Gamma$ . Other possibilities involve the approximation of  $H_2$  as a rigid rotor, which neglects the dependence of  $\Gamma$  on  $r$  and also vibrational-translational coupling. Future work should help distinguish between these possibilities.

#### IV. Summary

The present investigation indicates that the method used to calculate the energy surface and width for  $\text{He}(2^3\text{S})-\text{H}_2$  is reasonably accurate. Application of this method to other small molecules should be straightforward. Many interesting problems in the dynamics of collisional autoionization, however, remain unanswered. The present work has dealt with the quantum mechanical calculation of total ionization cross sections in the framework of a non-reactive, two-body collision. The extension to possibly reactive phenomena, and the calculation of branching ratios between various possible final ionization channels, has already been attempted by classical trajectory techniques. The assessment of this technique, and the investigation of possible quantum effects, will be an important area of future research.

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- \* Supported in part by the U. S. Energy Research and Development Administration, and by the National Science Foundation under grant GP-41509X.
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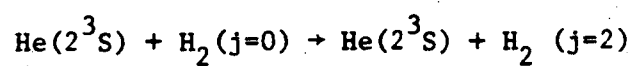
Table 1. Legendre expansion coefficients of the potential energy surface and width, in atomic units.

$R(a_0)$	$v_0$	$v_2$	$v_4$	$\Gamma_0$	$\Gamma_2$
3	.065113	.029598		$3.67 \times 10^{-3}$	$7.20 \times 10^{-4}$
4	.015107	.007986	.000685	$1.59 \times 10^{-3}$	$3.09 \times 10^{-4}$
5	.006416	.002679	.000206	$3.39 \times 10^{-4}$	$9.44 \times 10^{-5}$
6	.003315	.000922	.000047	$5.62 \times 10^{-5}$	$1.41 \times 10^{-5}$
7	.001533	.000277	-.000002	$8.52 \times 10^{-6}$	$1.92 \times 10^{-6}$
8	.000609	.000059	-.000010	$1.25 \times 10^{-6}$	$3.31 \times 10^{-7}$
9	.000199	-.000005		$1.82 \times 10^{-7}$	$6.40 \times 10^{-8}$
10	.000049	-.000012	-.000004	$2.42 \times 10^{-8}$	$1.21 \times 10^{-8}$

Table 2. Total ionization cross sections as a function of energy for  
 $\text{He}(2^3\text{S})-\text{H}_2$

E(eV)	$\sigma_1(\text{a}_0^2)$
0.010	.34
0.040	1.6
0.070	3.5
0.100	6.4
0.140	11.
0.200	20.
0.300	30.
0.400	35.
0.500	39.

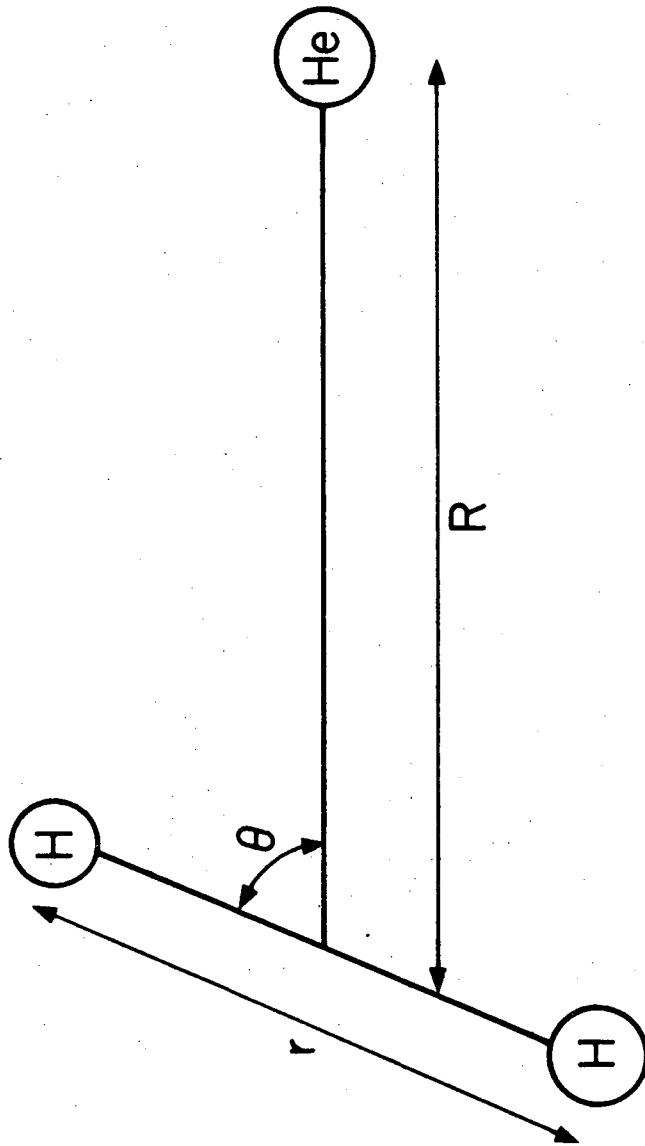
Table 3. Cross sections for the rotationally inelastic process



E(eV)	$\sigma_{0 \rightarrow 2}$ ( $a_0^2$ )
0.070	0.10
0.100	0.63
0.140	2.2
0.200	5.3

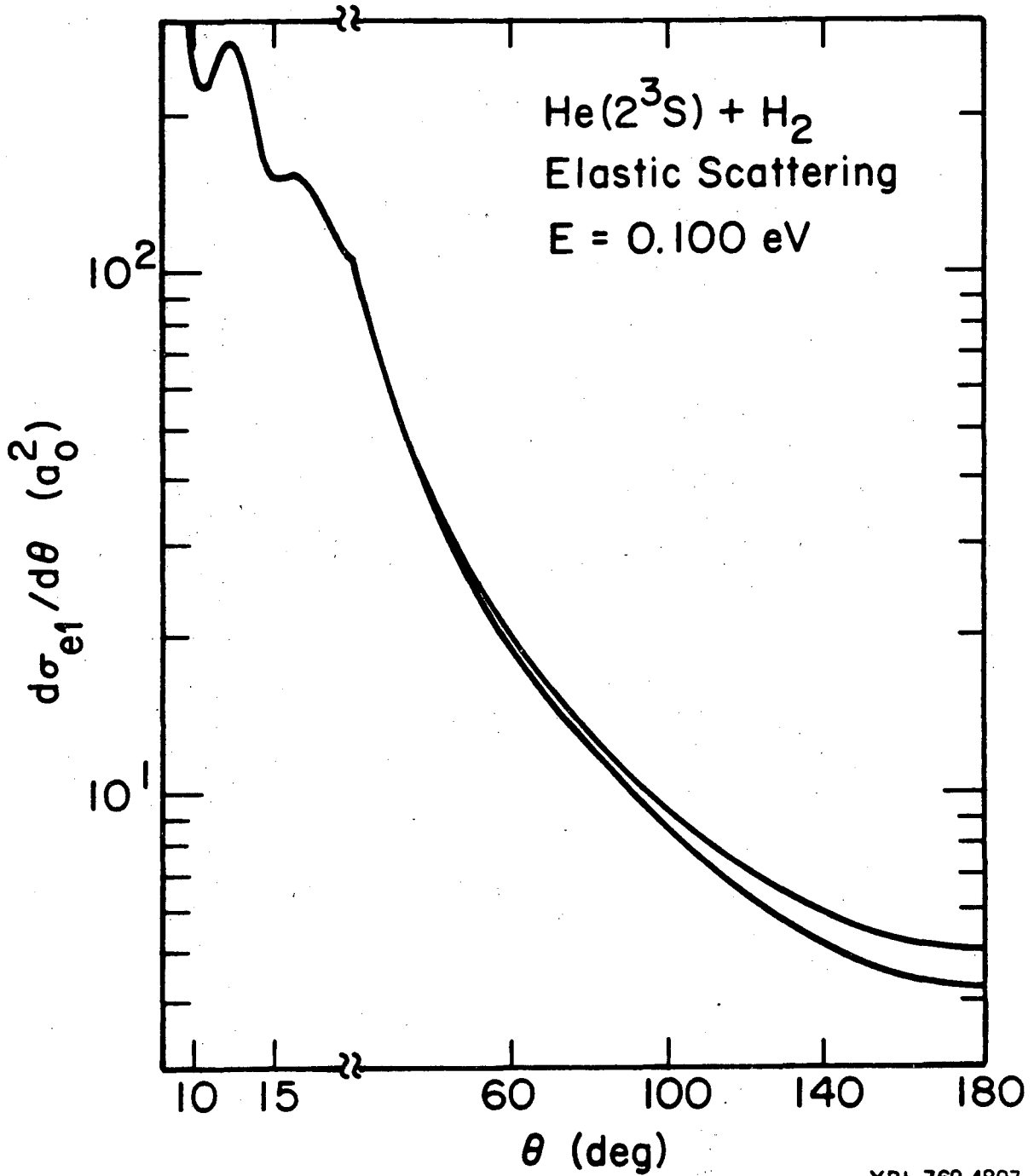
## Figure Captions

- Figure 1. Geometry of the  $\text{He}(2^3\text{S})\text{-H}_2$  in terms of  $R$ ,  $\theta$ , and  $r$ .
- Figure 2. Differential elastic scattering cross sections for  $\text{He}(2^3\text{S}) + \text{H}_2$  at (c.m.) collision energy  $E = 0.100$  eV, assuming the initial and final rotational states of  $\text{H}_2$  are  $j = 0$ . The upper curve was calculated with  $V^*$  alone, while the lower curve was calculated with  $V^* - \frac{1}{2} \Gamma$ . The cusp at  $\theta = 20^\circ$  is due to the change in the horizontal scale.
- Figure 3. Rate constants for the ionization of  $\text{H}_2$  by  $\text{He}(2^3\text{S})$ . The present ab initio theoretical results (solid curve) are compared with the experimental values obtained by Lindinger et al.



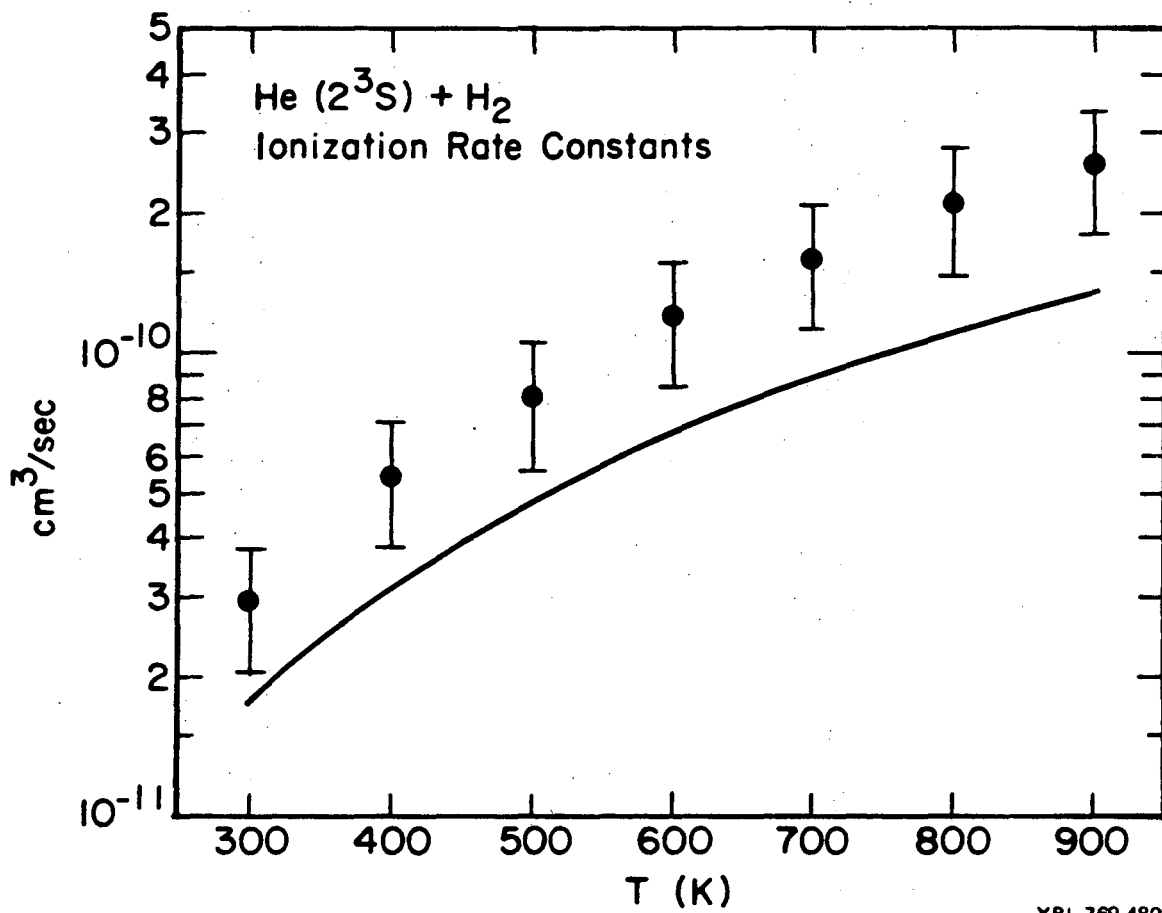
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Figure 1



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Figure 2



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Figure 3



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