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Penning and associative ionization of triplet metastable helium atoms*

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Potential energy curves for the $^1\Sigma_g^+$, $^3\Sigma_u^+$, and $^5\Sigma_g^+$ states which arise from two triplet metastable helium atoms ($1s\,2s\,^3S$) have been calculated by a large configuration interaction expansion. From the potential curves for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ autoionizing states, cross section for Penning and associative ionization have been calculated; the total ionization cross section for thermal energy (0.026 eV) collisions, for example, is computed to be 94 Å^2. In this low energy region the orbiting model is seen to be adequate for determining the total ionization cross section, but not the more specific cross sections.

I. INTRODUCTION

The triplet metastable state of helium $1s2s^3S$ is an important constituent of the helium afterglow.[1] It is through Penning ionization by helium metastables that ions of other species are produced:

$$He^* + X \rightarrow He + X^+ + e^- , \tag{1}$$

where He denotes the ground state of helium and He* the triplet metastable state. At sufficiently high concentrations the self-destruction of the triplet metastable, i.e.,

$$He^* + He^* \rightarrow He + He^+ + e^- \tag{2a}$$

$$\rightarrow He_2^+ + e^- , \tag{2b}$$

becomes significant and is an important mechanism for loss of metastables as well as production of the atomic and molecular ions He^+ and He_2^+.

This paper reports calculations of the potential curves arising from two triplet metastable helium atoms and the cross sections for the Penning and associative ionization reactions in Eq. (2). An earlier calculation by von Roos[2] gave an unreasonably small value (~0.01 Å^2) for the cross section, and a subsequent attempt by Klein[3] at calculating the relevant potential curves met with only partial success.

Section II describes the calculation of the $^1\Sigma_g^+$, $^3\Sigma_u^+$, and $^5\Sigma_g^+$ potential curves which arise from the two ^3S helium atoms; since He_2^+ and e^- can combine to give only a singlet and triplet continuum, the quintet state is actually a bound, nonautoionizing electronic state. The $^1\Sigma_g^+$ and $^3\Sigma_u^+$ autoionizing states were obtained in our configuration interaction calculation as before,[4] by selecting the eigenvalues of the electronic Hamiltonian matrix which dissociates to the correct separated atom limit. There is now ample justification,[5] both formal and practical, that a calculation such as this actually does describe the energy of autoionizing electronic states.

Section III summarizes the appropriate collision theory and presents calculations of the cross sections for Reaction (2). The total ionization cross section, and the fraction of which is the molecular product He_2^+, is calculated for collision energies from 0.01 eV to 0.30 eV; at 0.026 eV, for example, the total ionization cross section is 94 Å^2, ~70% of which leads to He_2^+. For the collision energy 0.03 eV the distribution of associative product in the rotational and vibrational states of He_2^+ is calculated (high vibrational states are populated), and the energy distribution of the ejected electron is also determined.

II. POTENTIAL CURVES

A. Methodology

The electronic structure calculations were intended to be as similar as possible to the HeH calculations reported earlier.[4] The double-zeta-plus-polarization basis set[6] of Slater functions employed is seen in Table I. The 1s functions and the 2p function with $\zeta = 0.8$ were optimized for the $^5\Sigma_g^+$ state of He_2, while the remaining functions were taken from the work of Miller and Schaefer.[4]

In analogy with the earlier HeH calculations, it would have been desirable to perform full configuration interaction (CI) calculations on the $^1\Sigma_g^+$, $^3\Sigma_u^+$, and $^5\Sigma_g^+$ states of He_2. In practice, however, full CI was only carried out for the $^5\Sigma_g^+$ state, for which there are 472 configurations. The $^5\Sigma_g^+$ calculations were relatively simple, since the state of interest (arising from ^3S He + ^3S He) is the lowest eigenvalue

TABLE I. Basis set of Slater functions centered on each He atom.

Type	Orbital exponent ζ
1s	2.011
1s	1.223
2s	0.65
2s	0.45
2p	0.80
2p	0.50

of this symmetry. The computations were carried out as described elsewhere.[7,8] Earlier calculations on the $^5\Sigma_g^+$ state of He_2 were reported by Klein[3] using the valence bond CI approach of Browne and Matsen.[9] The two calculated potential curves are similar the present results yielding total energies roughly 0.004 hartree ≈ 0.1 eV lower than Klein's near the preducted minimum.

For the autoionizing $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states it was not economical to carry out full CI calculations. The problem lies not with the size of the matrices (1888 configurations for $^3\Sigma_u^+$), but rather with the fact that the two states of interest are *not* the lowest (or even the 2nd, 3rd, or 4th lowest) energy eigenvalues of their respective symmetries. At the time of the computations, the problem of extracting the 20th eigenvalue and eigenvector of a 2000×2000 matrix was beyond our capabilities.

Therefore, it was decided to do limited CI based on a set of orbitals believed appropriate for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of He_2. The chosen orbitals were the natural orbitals (NO's) for the $^5\Sigma_g^+$ state. Our reasoning was that these three states, describing the interaction between metastable He atoms, should have rather similar natural orbitals. Since the $^5\Sigma_g^+$ calculations were full CI's, the natural orbitals obtained are the exact NO's within the chosen basis. In addition to allowing us to carry out a limited CI meaningfully, the use of natural orbitals is an important aid in locating (among the eigenvalues) each autoionizing state, i.e., the bound state embedded in a continuum.

For the $^1\Sigma_g^+$ state, preliminary calculations showed that two configurations, $1\sigma_g^2 2\sigma_g^2$ and $1\sigma_u^2 2\sigma_g^2$, dominated the wavefunction. Therefore, our CI was taken to include all configurations differing by one or two orbitals from these two reference configurations. 230 $^1\Sigma_g^+$ configurations are obtained in this way. The autoionizing He*–He* singlet state turns out to be the 10th eigenvalue with this basis set and configuration selection. The 10th eigenvalue has an energy appropriate to ^3S He + ^3S He at internuclear separation $R = 20$ bohr, and has the electronic structure expected for the $^1\Sigma_g^+$ state.

The proper dissociation of the $^1\Sigma_g^+$ molecular wavefunction to Hartree–Fock wavefunctions for two $1s2s\,^3S$ He atoms requires five configurations: $1\sigma_g^2 2\sigma_g^2$, $1\sigma_u^2 2\sigma_g^2$, $1\sigma_g 1\sigma_u 2\sigma_g 2\sigma_u$, $1\sigma_u^2 2\sigma_u^2$, and $1\sigma_g^2 2\sigma_u^2$. To test the adequacy of the configuration selection described in the previous paragraph, a CI wavefunction including the 436 single and double excitations obtained with respect to the above five reference configurations was constructed. Judiciously choosing 400 of these configurations, computations were carried out near the predicted minimum (R = 6 bohr) at a large separation (R = 12 bohr). The dissociation energy obtained in this way was 0.09 eV less than that found from the 230 configuration calculation described in the previous paragraph. From this test, it was decided that the 230 configuration calculation probably provides a qualitatively reasonable potential energy curve for the $^1\Sigma_g^+$ autoionizing state.

The $^3\Sigma_u^+$ wavefunction is dominated by a single configuration, $1\sigma_g 1\sigma_u 2\sigma_g^2$. Therefore, all 272 configurations differing by one or two orbitals from this reference configuration were included in the $^3\Sigma_u^+$ CI calculations. Again the natural orbitals from the $^5\Sigma_g^+$ full CI calculations were employed. In this basis, the autoionizing $^3\Sigma_u^+$ state is found to be the ninth energy eigenvalue of its symmetry.

One of the purposes of a study such as the present one is to gain some understanding of the electronic structure of autoionizing states. For this reason we give in Table II the coefficients of the most important configurations in the three wavefunctions. In addition the results of Table II sup-

TABLE II. Important configurations for those states of He_2 arising from two ^3S He metastables. Included are only those configurations with coefficient ≥ 0.3 for at least one of the three separations.

	$R=6$	$R=8$	$R=20$
$^1\Sigma_g^+$ state			
$1\sigma_g^2 2\sigma_g^2$	0.6065	0.5621	0.4070
$1\sigma_u^2 2\sigma_g^2$	0.6066	0.5626	0.4068
$1\sigma_g^2 2\sigma_u^2$	0.0868	0.1722	0.4358
$1\sigma_u^2 2\sigma_u^2$	0.0870	0.1722	0.4357
$1\sigma_g 1\sigma_u 2\sigma_g 2\sigma_u$	0.2015	0.2506	0.3777
$^3\Sigma_u^+$ state			
$1\sigma_g 1\sigma_u 2\sigma_g^2$	0.8290	0.7660	0.5303
$1\sigma_g 1\sigma_u 2\sigma_u^2$	0.1092	0.2239	0.5793
$1\sigma_g^2 2\sigma_g 2\sigma_u$	0.1801	0.2328	0.3431
$1\sigma_u^2 2\sigma_g 2\sigma_u$	0.1800	0.2328	0.3430
$1\sigma_g 1\sigma_u 2\sigma_g 3\sigma_g$	0.2441	0.3204	0.2513
$^5\Sigma_g^+$ state			
$1\sigma_g 1\sigma_u 2\sigma_g 2\sigma_u$	0.9851	0.9690	0.9144
$1\sigma_g 1\sigma_u 2\sigma_g 3\sigma_g$	0.1335	0.1254	0.3337

port the decisions made in the selection of configurations for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ calculations.

B. Potential Energy Curves

Figure 1 shows the *ab initio* potential curves for the states arising from $He^*(1s2s^3S)+He^*$. Also shown there is a Morse curve for the $^2\Sigma_u^+$ ground state of He_2^+. For the dissociation energy D_e, we used the very accurate *ab initio* value 2.469 eV determined by Liu.[10] The bond distance, $r_e = 2.044$ bohr, was also taken from Liu, while $\omega_e = 1698.5$ cm^{-1} was taken from the compilation of Rosen.[11]

As seen in Fig. 1, the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ potential curves are almost identical, having r_e and D_e values equal to 6.34 a_0 and 0.56 eV, and 6.27 a_0 and 0.61 eV, respectively. (The nonautoionizing $^5\Sigma_g^+$ state has a much shallower well of 0.07 eV at $r_e = 7.91$ a_0.) A qualitative explanation of this similarity between the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ potential curves is that they both correspond to the outer 2*s* electrons, which primarily determine the interaction potential, being singlet coupled (see Table II), and differ only in having the inner 1*s* electrons singlet and triplet coupled, respectively. Because of this similarity of the two potential curves (the difference between them is less than the reliability of our calculation), the $^3\Sigma_u^+$ potential was used in the calculations discussed in Sec. III. B to describe both the $^3\Sigma_u^+$ and $^1\Sigma_g^+$ potential curves.

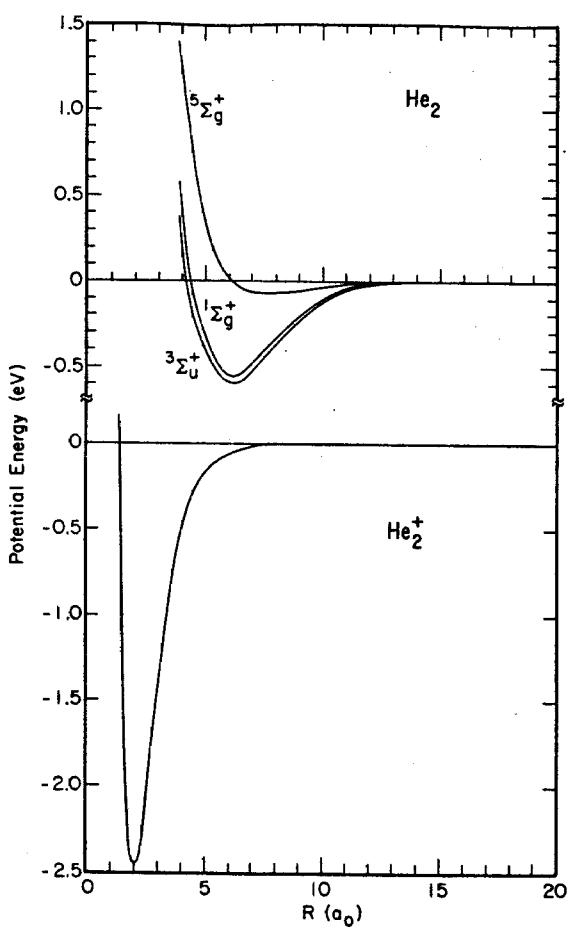

FIG. 1. Potential energy curves for the ground state of He_2^+ and the states of He_2 arising from two $1s2s^3$ He atomic states.

III. CROSS SECTIONS

A. Theory

To describe the Penning reaction

$$A^* + B \rightarrow A + B^+ + e^- \tag{3}$$

within a Born–Oppenheimer framework, three independent molecular functions are required: $V_0(R)$, the diatomic potential curve for A^*-B; $V_+(R)$, the diatomic potential curve for $A-B^+$; and $\Gamma(R)$, the autoionization width (rate of autoionization $=\Gamma/\hbar$) as a function of internuclear separation. The calculation of these quantities is a problem in electronic structure. Within a classical, or semiclassical version of the theory,[12] all collision properties of Reaction (3) can be expressed in terms of $V_0(R)$, $V_+(R)$, and $\Gamma(R)$.

An important intermediate quantity constructed from $V_0(R)$ and $\Gamma(R)$ is the probability function

$$P_b(R) = [\Gamma(R)/\hbar v_b(R)]\, 2\cosh\{\int_{R_0}^{R} dR'[\Gamma(R')/\hbar v_b(R')]\} \times \exp\{-\int_{R_0}^{\infty} dR'[\Gamma(R')/\hbar v_b(R')]\}\,, \tag{4}$$

where b is the impact parameter, R_0 the classical turning point, and $v_b(R)$ the local velocity:

$$v_b(R) = v[1 - V_0(R)/E - b^2/R^2]^{1/2}\,, \tag{5}$$

v being the initial relative velocity of A^* and B. $P_b(R)$ in Eq. (4) is the probability density for autoionization occurring at internuclear distance R. The total ionization probability for impact parameter b is therefore

$$P_b = \int_{R_0}^{\infty} dR P_b(R)\,, \tag{6}$$

and from Eq. (4) one can show that

$$P_b = 1 - \exp\{-2\int_{R_0}^{\infty} dR[\Gamma(R)/\hbar v_b(R)]\}\,; \tag{7}$$

the total ionization cross section is then given in this classical version of the theory by

$$\sigma_{tot} = 2\pi\int_0^{\infty} dbbP_b\,. \tag{8}$$

To determine the partitioning of σ_{tot} between atomic ($A+B^+$) and molecular (AB^+) products it is necessary to determine whether the final relative energy of A and B^+ corresponds to bound or to dissociated species. Within the Born–Oppenheimer approximation for separating electronic and nuclear motion, autoionization conserves the local kinetic energy of the nuclei, so that autoionization which occurs at internuclear distance R corresponds to

a final relative energy for A and B* [relative to $V_+(\infty)$] of

$$E_{AB^+} = E - V_0(R) + V_+(R) \,. \tag{9}$$

Ignoring tunneling, this will correspond to the molecular ion AB* if

$$E_{AB^+} \le V_+^{\max}(b) \tag{10a}$$

and

$$R \le R_{\max}(b) \,, \tag{10b}$$

where $V_+^{\max}(b)$ is the relative maximum of the effective potential

$$V_+(R) + Eb^2/R^2 \,,$$

and $R_{\max}(b)$ is the value of R at which this maximum occurs. The probability of *associative ionization*, i.e., the formation of the molecular ion, at impact parameter b is thus given by

$$P_b^{AI} = \int_{R_0}^{R_{\max}(b)} dR P_b(R) h[V_+^{\max}(b) - E + V_0(R) - V_+(R)] \,, \tag{11}$$

where $h(x)$ is the step function

$$h(x) = 1, \; x > 0$$
$$= 0, \; x < 0 \,.$$

The cross section for associative ionization is

$$\sigma_{AI} = 2\pi \int_0^\infty db b P_b^{AI} \,. \tag{12}$$

Regarding the product of associative ionization, it may be desirable in some cases to know the cross section for forming AB* in particular vibrational–rotational states (n,j). Within the classical version of the theory[12] it is not difficult to show that these cross sections are given by

$$\sigma_{nj} = \frac{\pi}{k^2} \frac{\partial W(n,j)}{\partial n} \sum_i \frac{P_b(R_i)}{|V_0'(R_i) - V_+'(R_i)|} \,, \tag{13}$$

where $k = (2\mu E/\hbar^2)^{1/2}$, $b = (j + \frac{1}{2})/k$, and $R_i \equiv R_i(n,j)$ are the roots of

$$V_0(R) - V_+(R) = E - W(n,j) \,, \tag{14}$$

$W(n,j)$ being the vibrational–rotational eigenvalues of AB* [referred to $V_+(\infty)$]; there are usually one or two such roots. It is clear that

$$\int dn \int dj (2j+1) \sigma_{nj} = \sigma_{tot} \,,$$

where σ_{tot} is the total ionization cross section.

If one focuses attention on the ionized electron[13] rather than the product atomic and molecular ions, then the quantity of interest is $\sigma(\epsilon)$ the cross section per unit energy for the ionized electron having an asymptotic energy ϵ. For autoionization at internuclear distance R the asymptotic kinetic energy of the electron is $\epsilon(R)$,

$$\epsilon(R) = \epsilon_\infty + V_0(R) - V_+(R) \,, \tag{15}$$

where ϵ_∞ is the excitation energy of A minus the ionization potential of B. The probability distribution in electron energy ϵ is thus related to the probability distribution in R,

$$P_b(\epsilon) d\epsilon = P_b(R) dR \,,$$

so that

$$P_b(\epsilon) = \sum_i P_b(R_i) / |V_0'(R_i) - V_+'(R_i)| \,, \tag{16}$$

where $R_i \equiv R_i(\epsilon)$ are the roots (there being either one or two) of the equation

$$\epsilon = \epsilon_\infty + V_0(R) - V_+(R) \,;$$

i.e., $R_i(\epsilon)$ are the two branches of the inverse function of $\epsilon(R)$ [Eq. (15)]. The cross section $\sigma(\epsilon)$ is given by

$$\sigma(\epsilon) = 2\pi \int_0^\infty db b P_b(\epsilon) \,, \tag{17}$$

and it is easy to see that

$$\int d\epsilon \sigma(\epsilon) = \sigma_{tot} \,.$$

The above expressions all require explicit knowledge of the width function $\Gamma(R)$, but this is unfortunately the most difficult quantity to calculate from first principles. Approximate models which do not require $\Gamma(R)$ are thus attractive. One such model which is not altogether unreasonable at low collision energy with systems for which $V_0(R)$ has an attractive well is the *orbiting model*[14,15,4]; the essential idea is that autoionization is said to occur if, and only if, the collision energy E is greater than the relative maximum in the effective radial potential. The total ionization cross section is given in this model by[4]

$$\sigma_{tot}(E) = \pi R^2 [1 - V_0(R)/E] \,, \tag{18a}$$

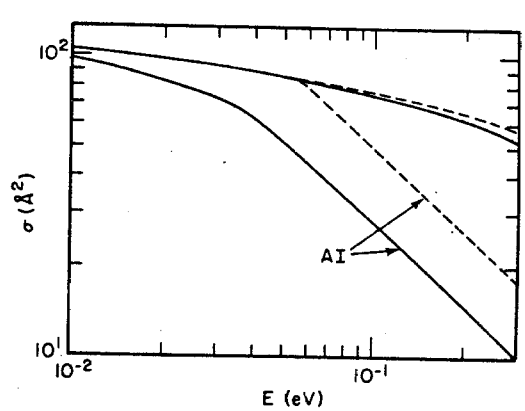

FIG. 2. The total ionization cross section (top curves) for the collision of two triplet metastable ($1s2s\,^3S$) helium atoms, and the component of which leads to He_2^+ (lower curves labeled AI), as a function of the relative collision energy. The broken curves are the results given by the orbiting model.

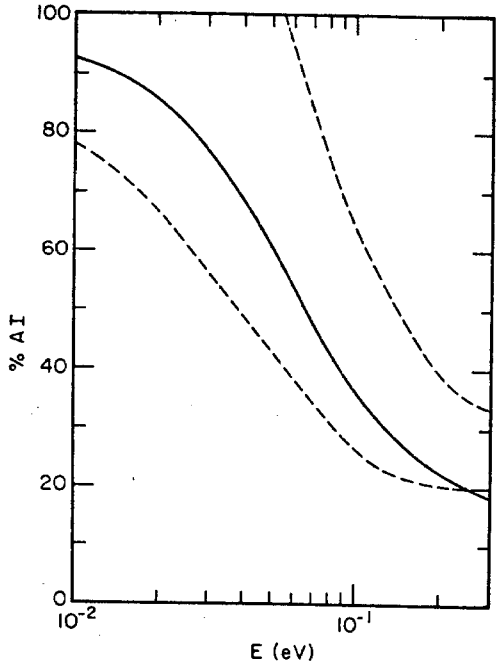

FIG. 3. The fraction of ionized products that are molecular ions, as a function of the relative collision energy. The upper broken line is the result of the orbiting model, and the lower broken line results with the value $R_0 = 0.762\ a_0$ in the width function [Eq (21)].

where $R = R(E)$ is the larger root of the equation

$$E = V_0(R) + \tfrac{1}{2} R V_0'(R)\ . \tag{18b}$$

To construct the more detailed cross sections within the orbiting model it is necessary to postulate *where* the autoionization occurs. Without introducing additional parameters into the model the only obvious choice is to assume that autoionization occurs at the classical turning point, i.e., the probability function of Eq. (4) is taken to be

$$P_b(R) = \delta[R - R_0(b,E)]\, h[B(E) - b]\ , \tag{19}$$

where $R_0(b,E)$ is the classical turning point, and $B(E)$ is the impact parameter for orbiting. With this form for $P_b(R)$ all of the more detailed cross sections can now be evaluated; the cross section for associative ionization, for example, is given in the orbiting model by

$$\sigma_{AI}(E) = \pi R^2 [1 - V_0(R)/E]\ , \tag{20a}$$

where here $R = R(E)$ is the root of the equation

$$E = V_0(R) + \tfrac{1}{2} R V_0'(R)\ . \tag{20b}$$

B. Results

As discussed in Sec. II.B, the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ potential curves are taken to be the same, so the calculation of cross sections proceeds as though there were just one autoionizing state with a statistical factor of $(1+3)/(1+3+5) = \frac{4}{9}$, by which all the cross section formulas of Sec. III.A must be multiplied. To further simplify the present calculations the autoionization width $\Gamma(R)$ was not calculated from first principles but simply taken to be a reasonable function,

$$\Gamma(R) = A e^{-R/R_0}\ ; \tag{21}$$

this form has been seen to fit the width calculated by Miller, Solcomb and Schaefer[16] for the He*–H system quite well, and the mechanism for autoionization in both of these systems is electron exchange. For He*–H the parameters are $A \simeq 0.3$ hartree, $R_0 \simeq 0.762\ a_0$, and for the present He*–He* system we modified R_0 to be $1.086\ a_0$ so as to make $\Gamma(R)$ of longer range. For the present results, as seen before[16] for He*–H, the total ionization cross section is quite insensitive to $\Gamma(R)$, being given adequately by the orbiting model; the more detailed collision properties are, of course, more dependent on the width function.

Figure 2 shows the total ionization cross section for Reaction (2) as a function of the initial collision energy. Also shown in the component of the total cross section which leads to the molecular ion (i.e., associative ionization); as with the earlier He*–H work,[16] the orbiting model is seen to overestimate the amount of associative ionization severely. The associative fraction as a function of collision energy is shown in Fig. 3, and to see the sensitivity of this quantity to the width function the result is also shown for the parameter R_0 of Eq. (21) taken as $0.762\ a_0$.

Figure 4 shows some contours for the distribution of the associative product in the vibrational-rotational states of He_2^+ for the collision energy 0.03 eV. The distribution covers a broad range of rotational states, $j = 0 - 38$, and is concentrated in high vibrational states, $n = 10$–20; this distribution

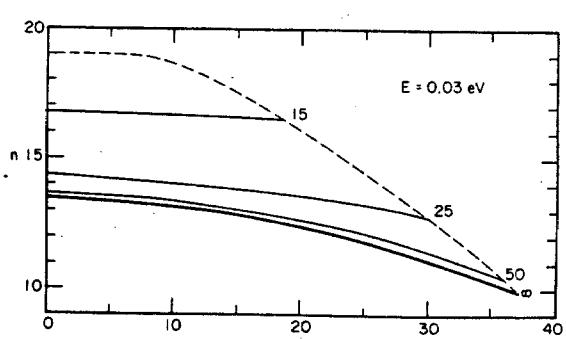

FIG. 4. Contours showing the distribution of associative product (He_2^+) in vibrational and rotational states n and j, respectively, as calculated from Eq. (13); units are 10^{-4} Å^2. The relative collision energy is 0.03 eV.

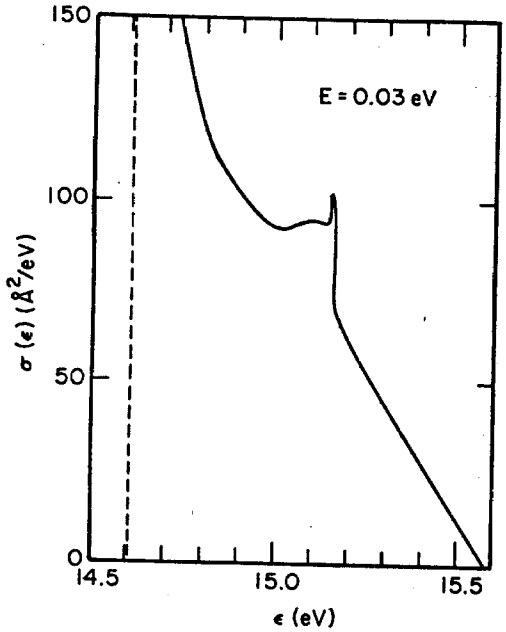

FIG. 5. The energy distribution of the ionized electron, as calculated from Eqs. (16)–(17), for the relative collision energy 0.03 eV. The broken vertical line indicates the position of the relative minimum of the function $\epsilon(R)$ [Eq. (15)].

in high vibrational states is fairly obvious from inspection of the potential curves in Fig. 1. Within the orbiting model, which allows autoionization only at the classical turning point, the distribution is a delta function along the heavy line in Fig. 4; the classical expression, Eq. (13), has a typical Jacobian infinity along this line but a finite distribution to higher vibrational states.

Finally, Fig. 5 shows the energy distribution of the ejected electron for an initial collision energy of 0.03 eV. The low energy maximum results from the relative minimum of the quantity $\epsilon(R)$ [Eq. (15)], and the shoulder at $\epsilon \sim 15.1$ eV is associated with the asymptotic value ϵ_∞. These features are qualitatively the same as for the He*–H system.[16]

IV. DISCUSSION

Phelps and Molnar[17] have determined the total ionization cross section for Reaction (2) to be ~100 Å² at 300 °K, which agrees quite well with our value of 94 Å² at 0.026 eV collision energy. In a more recent experimental investigation, however, Johnson and Gerardo[18] conclude that the total ionization cross section at 300 °K should be ~250 Å². Our results obviously favor the earlier experimental value, particularly so in light of the fact that the orbiting model is operative for the *total* ionization cross section in this energy range; at worst the orbiting model would be expected to provide an *upper bound* to the total ionization cross section. Unless our potential curves are in substantial error, therefore, there seems little possibility of the cross section being larger than ~100° Å². (An orbiting model calculation[14] based on simply the long-range van der Waals potential $-C/R^6$ gives a value of 101 Å² at 300 °K.)

In this low energy region the total ionization cross section is insensitive to the width function, a fact which is fortunate if one's goal is to calculate the total ionization cross section, but which is unfortunate if one wishes to obtain information about the width from experimental determination of this quantity. As has been noted, however, the more detailed collision properties—the fraction of associative product and its distribution in vibrational–rotational states, and the energy distribution of the ejected electron—depend more sensitively on the width function, so that experimental determination of these quantities would give important information concerning the autoionization width.

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