

## Radiative deexcitation of singlet metastable helium by collisions with helium atoms

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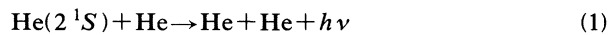
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(Received 23 July 1990)

Cross sections and rate coefficients are reported for the process  $\text{He}^*(2^1S) + \text{He} \rightarrow \text{He} + \text{He} + h\nu$ , for collision energies corresponding to gas temperatures in the range from 100 to 32 000 K.

### I. INTRODUCTION

In a previous paper<sup>1</sup> we discussed the classical, optical potential, and quantal distorted wave theories of collision-induced radiative deexcitation of metastable  $\text{He}(2^1S)$ . The cross sections and rate coefficients were calculated for the process



for collision energies corresponding to a range of gas temperature from 250 to 32 000 K. In that calculation we used the transition dipole moment given by Allison, Browne, and Dalgarno,<sup>2</sup> and pointed out that the accuracy of the reported cross sections is limited by the uncertainty in this dipole moment.

In this Brief Report we calculate the cross sections for process (1) using an improved transition dipole moment. In Sec. II we give a brief review of the theoretical method<sup>1</sup> used in the present calculation. A discussion and the results are reported in Sec. III.

### II. THEORY

Accurate total radiative emission cross section (integrated over all photon wavelengths) for process (1) can be obtained using the local optical potential method.<sup>1</sup> In this method, the initial approach of the  $\text{He}^*(2^1S) + \text{He}$  collision partners is described by the wave equation

$$\left[ \frac{-1}{2\mu} \nabla_{\mathbf{R}}^2 + V(\mathbf{R}) - E \right] F(\mathbf{R}) = \frac{i}{2} A(R) F(\mathbf{R}), \quad (2)$$

where  $\mathbf{R}$  is the internuclear separation vector,  $\mu$  is the reduced mass,  $V(\mathbf{R})$  is the Born-Oppenheimer potential curve of the  $A^1\Sigma_u^+$  state of the  $\text{He}_2$  system, and

$$A(R) = \frac{4}{3c^3} D^2(R) |\Delta E(R)|^3 \quad (3)$$

is the radial-dependent, radiative transition probability.  $D(R)$  is the radial transition dipole moment of the  $A^1\Sigma_u^+$  and  $X^1\Sigma_g^+$  states, and  $\Delta E(R)$  is the energy difference between the two molecular potential curves.

Equation (2) may be solved using a coupled equation approach.<sup>3</sup> However, because the right-hand side of (2) is small, a distorted-wave approach<sup>1</sup> can be exploited to obtain highly accurate phase shifts. In this method the wave function  $F(\mathbf{R})$  is expressed as a partial-wave expansion, and the imaginary part of the complex phase shift,

for the  $J$ th partial wave, is given by<sup>1</sup>

$$\eta_J = \frac{\pi\mu}{2k_a} \int_0^\infty dR |s_J(k_a R)|^2 A(R), \quad (4)$$

where  $k_a \equiv \sqrt{2\mu[E - V(\infty)]}$  is the wave number of the system during the initial approach and  $s_J(k_a R)/R$  is the regular solution, for the  $J$ th partial wave, to the radial component of the homogeneous equation corresponding to (2) [i.e., the right-hand side of (2) is set to zero]. It has the asymptotic form

$$s_J(k_a R) \rightarrow \left[ \frac{2}{\pi} \right]^{1/2} \sin \left[ k_a R - \frac{J\pi}{2} + \delta_J(a) \right], \quad (5)$$

where  $\delta_J(a)$  is the real, elastic scattering phase shift. The total cross section for the transition cross section is given by<sup>1</sup>

$$\sigma = \frac{\pi}{k_a^2} \sum_J (2J+1) [1 - \exp(-4\eta_J)]. \quad (6)$$

The sum over partial waves is restricted to odd values of  $J$ , in order to ensure the correct symmetry of the nuclear wave function.<sup>1</sup> Because the  $\text{He}(2^1S) + \text{He}(1^1S)$  channel is a linear combination of the  $A^1\Sigma_u^+$  and  $C^1\Sigma_g^+$  states, the latter of which cannot make a transition into the final, ground, gerade state of the  $\text{He}_2$  system, a statistical factor of  $\frac{1}{2}$  is incorporated in the derivation of (6).

### III. RESULTS AND DISCUSSION

In the previous paper<sup>1</sup> we compared the calculated cross sections for (1) using both *ab initio* and semiempirical  $A^1\Sigma_u^+$  potential curves available in the literature.<sup>4,5</sup> We found that the cross sections are quite sensitive to the height of the potential barrier hump<sup>6</sup> in the  $A^1\Sigma_u^+$  potential at large internuclear distances. A discrepancy in the calculated value of the barrier height, between the *ab initio* and semiempirical theories,<sup>4,5,7</sup> has been resolved by the *ab initio* calculation of Yarkony.<sup>8</sup> He obtained a value of  $R_b = 5.93a_0$  for the location of the barrier maximum and a value of  $V_b = 47.48$  meV for its height. These values are consistent with the semiempirical values  $R_b = 5.92a_0$  and  $V_b = 50.02$  meV, given by Jordan and Siska,<sup>4</sup> and the values  $R_b = 5.86a_0$  and  $V_b = 47.0$  given by Brutschy and Halberland.<sup>7</sup> In this calculation we use the semiempirical potential curve for the  $A^1\Sigma_u^+$  state given by Jordan and Siska.<sup>4</sup> For the ground  $X^1\Sigma_g^+$  we use the

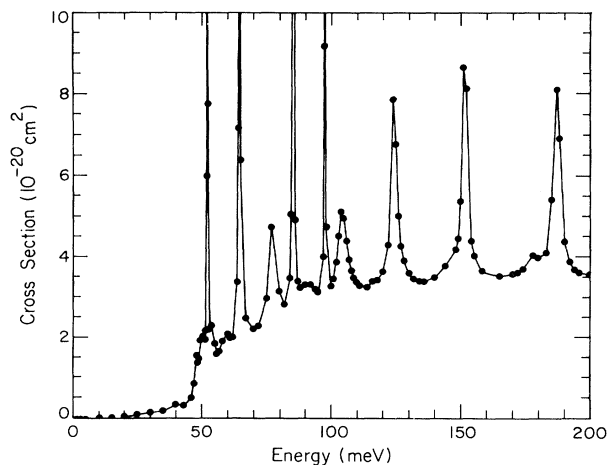


FIG. 1. Total cross section for process (1) as a function of relative collision energy (meV).

semiempirical potential of Sando and Dalgarno,<sup>9</sup> and adopt the radial transition dipole moment calculated by Yarkony.<sup>8</sup>

The result of the calculations is shown in Fig. 1. The resonance peaks in the cross section are due to quasi-bound vibrational levels supported by the  $A^1\Sigma_u^+$  state of the  $\text{He}_2$  system. This resonance structure is identical to the calculated values shown in Fig. 2 of Zygelman and Dalgarno.<sup>1</sup> The major difference between the previous calculated cross sections and the ones presented here is in their magnitudes. The latter ones, shown in Fig. 1, are considerably smaller than the ones given previously,<sup>1</sup> and reflect a significant difference in the radial transition dipole moments used in the two calculations. Although the qualitative features of the dipole moments are similar, the values given by Yarkony are somewhat smaller at larger internuclear distance than the ones given by Allison, Browne, and Dalgarno. At  $R = 6a_0$  Yarkony obtains the value  $|D| = 0.0977$ , whereas Allison, Browne, and Dalgarno obtain  $|D| = 0.17$  (in a.u.). For smaller internuclear distances the two dipole moments are in better agreement. The most significant contributions to the total quenching rate result from transitions occurring near the region of the local maximum of the hump, and the cross sections are sensitive to the value of the transition dipole moment in this region. Because the transition probability is proportional to the square of  $D(R)$ , we can estimate the ratio of the cross sections by evaluating the square of the ratio of the two dipole moments at  $R = 6a_0$ . This simple assumption gives ratios for the two calculated cross sections in qualitative agreement with the de-

TABLE I. Rate coefficients for process (1) at temperature  $T$ .

$T$ (K)	Rate ( $10^{-14} \text{ cm}^3 \text{ s}^{-1}$ )
100	0.010
200	0.130
300	0.306
500	0.627
1000	1.14
2000	1.61
4000	1.97
8000	2.20
16000	2.29
32000	2.29

tailed calculation.

In Table I we present the calculated rate coefficients assuming a Boltzmann distribution of velocities. At low temperatures the rates are considerably smaller than the ones calculated previously<sup>1</sup> and are in fortuitous agreement at low temperatures with the ones obtained by the semiclassical calculation of Allison, Browne, and Dalgarno.<sup>2</sup>

From absorption studies, Phelps<sup>10</sup> estimated the cross section for (1) to have a value of  $3 \times 10^{-20} \text{ cm}^2$ , which corresponds to a rate coefficient of  $k = 0.54 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  at room temperature. Payne *et al.*<sup>1</sup> measured the decay constant for the depopulation of  $\text{He}(2^1S)$  via process (1) to have the value  $\beta = 220P \text{ s}^{-1}$ , where  $P$  is the pressure, in Torr, of the helium gas. Using the ideal gas law and assuming room-temperature conditions, this decay constant gives a rate coefficient  $k = 0.68 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ . Although these experimental values compare well with our theoretical value of  $k = 0.31 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ , it is difficult to explain the remaining discrepancy in terms of uncertainties in the potential curves and the dipole coupling. Although the neglect of nonadiabatic effects in our theoretical framework seems well justified at low collision velocities, a calculation including such effects may be necessary in order to resolve the continued discrepancy between theory and experiment.

#### ACKNOWLEDGMENTS

I would like to thank A. Dalgarno for discussions and his continued interest in this work. I would also like to thank K. Kirby and A. Young for useful comments and discussion. This work was supported by U.S. Department of Energy, Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Research.

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