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Penning Ionization of H_2 by He^* :

Calculation of Anomalous Structure in the Singlet Interaction Potential*

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Recent experimental measurements^{1,2} of Penning ionization of several species, H_2 being one, by the singlet metastable state of helium ($1s2s^1S$) have indicated that there is a relative maximum in the interaction potential (cf. Fig. 1). This is somewhat mystifying since experiments with the triplet state of helium ($1s2s^3S$) do not imply interaction potentials with such a structure. If the "inner well" is thought to arise from an avoided crossing with the ionic state $He^+H_2^-$, for example, then it is not clear why it should affect the singlet interaction potential and not the triplet.

Hickman, Isaacson, and Miller³ have recently reported large scale configuration interaction calculations for the interaction potential of triplet He^* ($1s2s^3S$) and H_2 (and also the "width" of this state with respect to autoionization) which was used to compute cross sections for the Penning ionization reaction $He^* + H_2 \rightarrow He + H_2^+ + e^-$, etc. Related calculations have also been carried out by Cohen and Lane⁴ (see also Preston and Cohen⁵), but the interaction potentials were obtained from a much smaller (i.e., valence bond) configuration interaction expansion and also involved a single center approximation for H_2 . Rate constants computed with both of these triplet potentials^{3,4} agree reasonably well with experimental results, although the potential obtained by Haberland⁶ by fitting his molecular beam differential cross section measurements agrees much better

with that of Hickman et al.³. None of these triplet potentials, theoretical or experimental, show a relative maximum. Also, the anisotropy of both theoretical triplet potential energy surfaces^{3,4} is quite small, so that most aspects of the scattering can be analyzed by taking the interaction to be spherically symmetric.

This Communication reports our calculations⁷ for the singlet He^*-H_2 potential energy surface. Figure 1 shows that the potential curve for a perpendicular (C_{2v}) approach does have a relative maximum while that for a collinear ($C_{\infty v}$) approach does not. This singlet potential surface is much more anisotropic than the triplet one,³ however, so that the effective spherically symmetric potential (cf. Fig. 1) which Haberland⁶ obtained by fitting to his experimental data bears no simple relation to the true potential energy surface. It is interesting, and perhaps significant, that the height of the relative maximum of our C_{2v} potential is approximately the same as that of Haberland's⁶ effective potential, but a meaningful comparison between theory and experiment must await scattering calculations with the full anisotropic potential energy surface. These are in progress.

The physical origin of the structure in the singlet potential appears (from a preliminary analysis of our wavefunction) to be due to interaction between the two states that dissociate to $\text{He}^*(1s2s \ ^1S)-\text{H}_2$ and to $\text{He}^*(1s2p \ ^1P)-\text{H}_2$: for internuclear distances beyond the relative maximum the outer electron of helium is in essentially a 2s orbital, while for internuclear distances shorter than the relative maximum it is in an orbital roughly characterized as a 2s-2p hybrid. (The fact that the structure appears for C_{2v} geometry and not $C_{\infty v}$ indicates that it cannot be due to interaction with the ionic state He^+-H_2^- , because in C_{2v} the singlet and ionic

states are of different symmetry.) This same effect is seen in the interaction potentials computed by Slocomb et al.⁸ for the states arising from He($1s^2 \ ^1S$) and H($2s, 2p$); here the 2s and 2p states of H are degenerate so that s-p hybridization is induced at large internuclear distances and leads to an interaction potential with a sizable (~ 2.5 eV) well depth.

The "mechanism" leading to s-p hybridization can be understood in terms of the Demkov model^{9,10} used in electronically non-adiabatic scattering theory. A two-state approximation is assumed for the electronic Hamiltonian matrix $\{H_{i,j}\}$, $i, j = 2s, 2p$, and the Demkov model assumes that the matrix elements vary with internuclear distance as

$$|H_{2s,2s} - H_{2p,2p}| = \Delta\epsilon = \text{constant}$$

$$H_{2s,2p} = Ae^{-\lambda R}$$

For large R , $\Delta\epsilon \gg Ae^{-\lambda R}$ so that the Hamiltonian is diagonal in the 2s, 2p basis; for sufficiently small R , however, $\Delta\epsilon \ll Ae^{-\lambda R}$, and the Hamiltonian is diagonalized by a transformation to the states $2s \pm 2p$, i.e., s-p hybrids. The switch-over takes place in the region of R for which $|H_{2s,2s} - H_{2p,2p}| = 2|H_{2s,2p}|$, i.e., at $R = \lambda^{-1} \ln(2A/\Delta\epsilon)$.

This same type of interaction is also possible, of course, for the triplet interaction potential--the relevant states of helium in this case being $1s2s \ ^3S$ and $1s2p \ ^3P$ --but asymptotically the $1s2s \ ^3S - 1s2p \ ^3P$ separation is 1.14 eV, while that for $1s2s \ ^1S - 1s2p \ ^1P$ is only 0.60 eV. The Demkov model thus implies that s-p hybridization in the triplet case will not take place until smaller R (because $\Delta\epsilon$ is larger) where no attractive well

appears because the potential is too steeply repulsive.

The Demkov picture also provides a qualitative explanation of the anisotropy of the potential inside the relative maximum (cf. Fig. 1). s-p hybridization essentially places the 2s-2p electron on the opposite side of He from H₂, effectively bearing the +1 core of He to H₂. The interaction is thus qualitatively that of a charge-quadrupole, $V(R,\gamma) \sim -P_2(\cos\gamma)$, so that the perpendicular geometry is most stable. (The charge-quadrupole picture is not quantitative because of the small internuclear distance.)

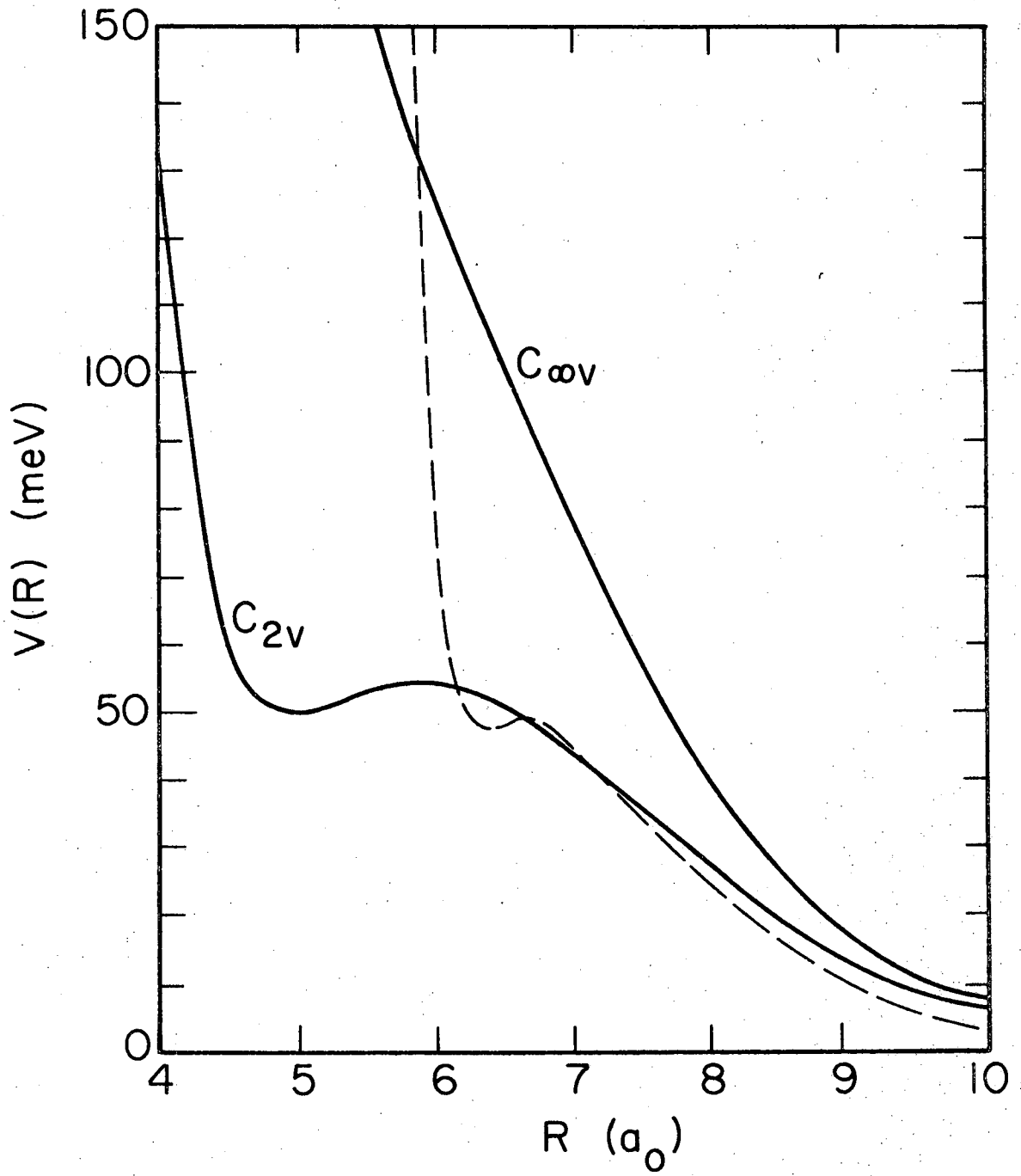
Calculation of the autoionization width for the singlet potential surface and cross sections for Penning ionization are in progress.

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Figure Caption

The two solid curves are the present results for the $\text{He}^*(1s2s\ ^1S)\text{-H}_2$ interaction potential for perpendicular (C_{2v}) and collinear ($C_{\infty v}$) approaches. R is the distance between He and the center of mass of H_2 , and the H-H distance is fixed at its equilibrium value $1.4 a_0$. The units of energy are milli-electron volts and of distance are Bohr radii. The dashed curve is the effective spherically symmetric potential of ref. 6.



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