

A surface hopping study of energy transfer in $\text{Na} + \text{Cd}^*$ collisions

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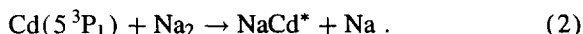
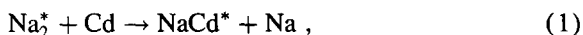
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Abstract

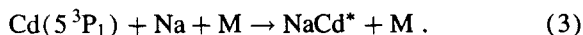
We have computed the cross sections for energy transfer and intramultiplet mixing in collisions between excited Cd and ground state Na atoms. Classical trajectories with surface hopping have been run on ab initio potentials, taking into account nonadiabatic and spin-orbit couplings. The theoretically determined cross sections contribute to identify the source of excited sodium atoms in heat pipe oven experiments with laser excitation of cadmium. The short lifetime of the collision complex leads to the conclusion that the three-body process $\text{Na} + \text{Cd}^* + \text{M} \rightarrow \text{NaCd}^* + \text{M}$ has a negligible role in the excimer production.

1. Introduction

The emission spectra of NaCd^* have been studied in heat-pipe oven experiments [1–5]. The excimer can be produced both from excited Na_2 or from Cd atoms in the $5p\ ^3P_1$ state. The two processes are, respectively,

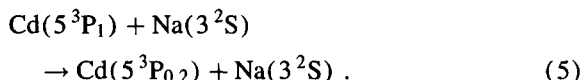
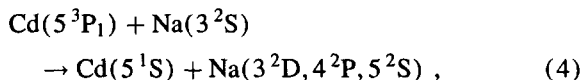


A three-body process has also been envisaged [4]:



The potential energy curves of the $\text{Na} + \text{Cd}$ system have been determined by ab initio calculations [6]. Spectral simulations have been run [7] on the basis of the ab initio results, in order to interpret the red and blue emission band systems of NaCd^* [1,2,4,5].

The observation of Na emission lines in Na–Cd vapor mixtures, irradiated at the resonance frequency of Cd (5^3P_1), implies the possibility of energy transfer from Cd^* to Na: however, several excited states of Na are populated, and it is reasonable to assume that not all of them are directly produced by collisions with Cd^* [8]. These observations prompted us to undertake the work presented here. We determined the cross sections for the processes



To this end, we run trajectory calculations with surface hopping [9,10] on ab initio potential energy curves [6], taking into account spin-orbit and nonadiabatic interactions.

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Table 1
Asymptotic and quasi-diabatic molecular states and energies

Molecular states		Asymptotic states		
$\Omega = \Lambda + \Sigma$	Hund's case b symbols	Na	Cd	energies (cm ⁻¹) [13]
1/2	$2\Sigma^+$	$3^2S_{1/2}$	5^1S_0	0
1/2	$2\Sigma^+, 2\Pi$	$3^2P_{1/2,3/2}$	5^1S_0	16956.2, 16973.4
3/2	2Π	$3^2P_{3/2}$	5^1S_0	16973.4
1/2	$2\Sigma^+$	$4^2S_{1/2}$	5^1S_0	25739.9
1/2	$2\Sigma^+, 2\Pi$	$3^2D_{3/2,5/2}$	5^1S_0	29172.9
3/2	$2\Pi, 2\Delta$	$3^2D_{3/2,5/2}$	5^1S_0	29172.9
5/2	2Δ	$3^2D_{5/2}$	5^1S_0	29172.9
1/2	$2\Sigma^+, 2\Pi$	$4^2P_{1/2,3/2}$	5^1S_0	30266.9, 30272.5
3/2	2Π	$4^2P_{3/2}$	5^1S_0	30272.5
1/2	$2\Sigma^+$	$5^2S_{1/2}$	5^1S_0	33200.7
1/2	$2,4\Sigma^+, 2,4\Pi$	$3^2S_{1/2}$	$5^3P_{0,1,2}$	30114.0, 30656.1, 31827.1
3/2	$4\Sigma^+, 2,4\Pi$	$3^2S_{1/2}$	$5^3P_{1,2}$	30656.1, 31827.1
5/2	4Π	$3^2S_{1/2}$	5^3P_2	31827.1

2. Surface hopping calculations and energy transfer cross sections

The details of the ab initio treatment on NaCd are given elsewhere [6]. Briefly, we ran quasi-degenerate perturbation theory (QDPT) calculations by the CIPSI algorithm, in a basis of quasi-diabatic states [11]. The quasi-diabatic states $|\eta_I\rangle$ are characterized as being approximately invariant with respect to changes in the internuclear distance, R . They can be identified with antisymmetrized products of atomic states: Na(3^2S) with Cd(5^3P), and Na($3^2S, 4^2S, 5^2S, 3^2P, 4^2P, 3^2D$) with Cd(5^1S), as detailed in Table 1. The QDPT treatment produces the matrix $\mathbf{H}^{(QDPT)}(R)$, representative of the electrostatic hamiltonian in the basis of the quasi-diabatic states. The diagonal matrix elements of $\mathbf{H}^{(QDPT)}(R)$ are shifted by constant amounts, in order to reproduce exactly the baricenters of the atomic multiplets.

The spin-orbit and dynamical (radial) couplings are introduced by two approximate procedures, exploiting the diabatic nature of the basis states. First, we assume that the spin-orbit hamiltonian is represented by the same matrix $\mathbf{H}^{(SO)}$ at all internuclear distances: the matrix elements are determined by the fine structure of the separate atoms. The theoretical justification of this approximation and its validity in reproducing the splitting of the $2^2\Pi$ state of NaCd observed in emission spectra, are discussed in Refs.

[6,7]. The total electronic hamiltonian, represented in the diabatic basis by the matrix \mathbf{H} , is the sum of the electrostatic and spin-orbit contributions:

$$\mathbf{H} = \mathbf{H}^{(QDPT)} + \mathbf{H}^{(SO)}. \quad (6)$$

The eigenvalues of the \mathbf{H} matrix, $E_K(R)$, are the adiabatic potential energy curves employed in the trajectory calculations.

The eigenvectors of \mathbf{H} represent the adiabatic states $|\psi_K\rangle$ in the quasi-diabatic basis:

$$\mathbf{H} \mathbf{C}_K = E_K \mathbf{C}_K, \quad (7)$$

$$|\psi_K\rangle = \{|\eta_1\rangle \dots |\eta_N\rangle\} \mathbf{C}_K. \quad (8)$$

In evaluating the radial nonadiabatic couplings we neglect the terms containing derivatives of the quasi-diabatic wavefunctions, $\langle \eta_I | \partial/\partial R | \eta_J \rangle$, and we retain only the "coefficient mixing" contribution [11,12]:

$$\begin{aligned} \langle \psi_K | \partial/\partial R | \psi_L \rangle &\simeq \mathbf{C}_K^\dagger \frac{\partial \mathbf{C}_L}{\partial R} \\ &= (E_L - E_K)^{-1} \mathbf{C}_K^\dagger \frac{\partial \mathbf{H}}{\partial R} \mathbf{C}_L. \end{aligned} \quad (9)$$

Notice that in this scheme (Hund's case a), certain crossings between states of different spin and space symmetry are treated as avoided crossings, because of the spin-orbit interaction: therefore, transitions between these states are governed by the radial couplings (9). We shall neglect the coupling of electronic and

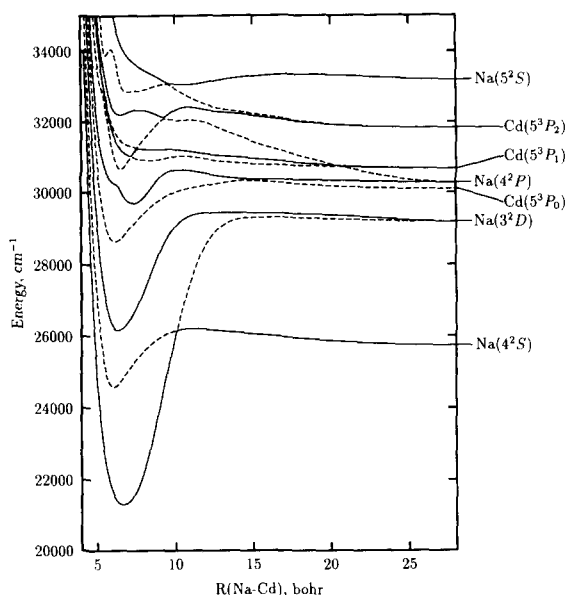


Fig. 1. Adiabatic potential energy curves of NaCd, including spin-orbit coupling. States with $\Omega = 1/2$. The three lowest states are omitted.

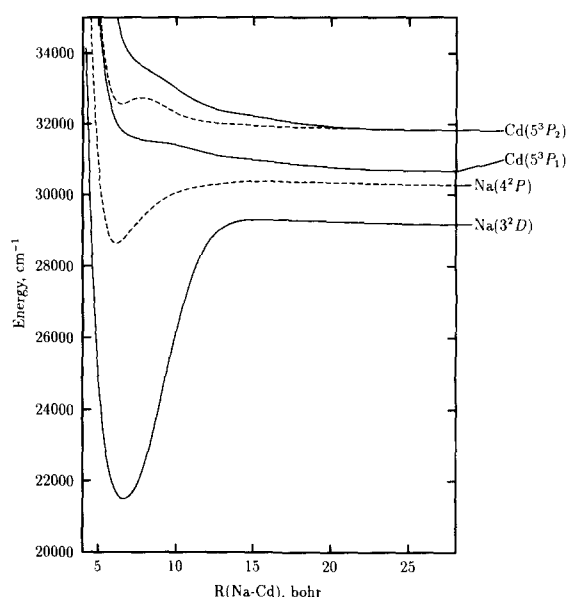


Fig. 2. Adiabatic potential energy curves of NaCd, including spin-orbit coupling. States with $\Omega = 3/2$. The lowest state is omitted.

nuclear angular momentum, therefore $\Omega = A + \Sigma$ is a good quantum number (here A and Σ are the projections of orbital and spin angular momentum on the internuclear axis). We have three possible values of $|\Omega|$, 1/2, 3/2 and 5/2: Table 1 shows how the electronic states are distributed in the three Ω manifolds. States with $\pm|\Omega|$ are degenerate, so we shall restrict ourselves to considering positive values of Ω . Figs. 1 and 2 show the adiabatic energies for $\Omega = 1/2$ and $\Omega = 3/2$, respectively. There is no contribution to $\Omega = 5/2$ from $\text{Cd}(5^3\text{P}_1)$, so we have no entrance channel to this manifold. All states up to $\text{Na}(5^2\text{S})$ have been included in the calculations.

Our implementation of Tully's surface hopping method [9,10] has been described in a previous paper [14]. We compute the final probabilities P_{KL} of ending up in the electronic state L when starting in K , as averages over many trajectories. For selected values of the initial relative kinetic energy E_T of the two atoms, we ran batches of trajectories with a variable impact parameter B . The B values were sampled so that the intervals where the contribution to the cross sections is largest (small B) are better represented: in averaging the final probabilities we weighted the

results with the correct distribution for B , $g(B) \propto B$.

The $\text{Cd}(5^3\text{P}_1)$ multiplet gives origin to two states with $\Omega = 1/2$ and one with $\Omega = 3/2$. As the initial state can be any of the three, with equal probabilities, the cross section for the production of state L is

$$\sigma_L(E_T) = \frac{1}{3} \sum_K P_{KL}(E_T), \quad (10)$$

where the index K runs over the three entrance channels. However, the contribution of the $\Omega = 3/2$ state is negligible, because all the crossings are strongly avoided in that manifold, so the transition probabilities are small.

The $\Omega = 1/2$ states are both slightly repulsive and they cross the $^2\Sigma^+$ curve originating from $\text{Na}(4^2\text{P})$ between $R = 20.4$ and 20.7 bohr. An expanded view of this region is shown in Fig. 3. The largest contribution to the cross section for the production of $\text{Na}(4^2\text{P})$ comes from these two crossings: as they lie about 70 and 100 cm^{-1} above the $\text{Cd}(5^3\text{P}_1)$ asymptote, the process needs a modest activation energy. Other crossings, located at much shorter distances ($R < 10$ bohr), lead to the production of $\text{Cd}(5^3\text{P}_0)$ and of $\text{Cd}(5^3\text{P}_2)$, without excitation of Na.

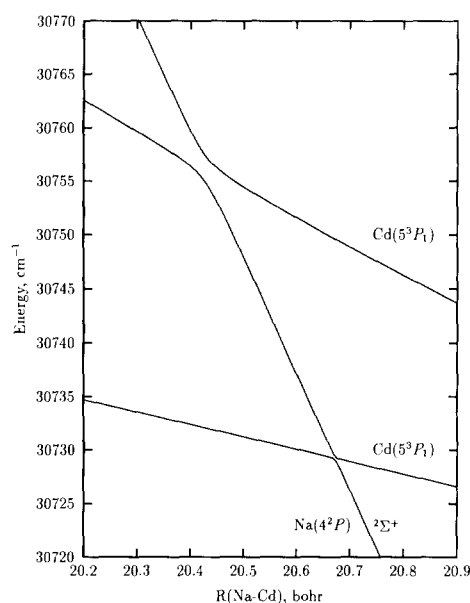


Fig. 3. An expanded view of the potential energy curves shown in figure 1 ($\Omega = 1/2$). The focus is on the region of the crossings between the $^2\Sigma^+$ state dissociating to $\text{Na}(4^2\text{P})$ and the two states originated by $\text{Cd}(5^3\text{P}_1)$.

The probability of all other transitions is small, because lower states are weakly coupled to the entrance channel, while the next higher state, $\text{Na}(5^2\text{S})$, is too high in energy to be populated by thermal processes. This is probably the most significant result of this study: as only $\text{Na}(4^2\text{P})$ can be populated directly by energy transfer, one should devise other mechanisms to explain the observation of emission from $\text{Na}(3^2\text{P}, 3^2\text{D}, 5^2\text{S} \text{ and } 4^2\text{D})$ [8].

Fig. 4 shows the cross sections as functions of the relative kinetic energy, E_T . The total cross sections at a given temperature are obtained by integrating over E_T the energy dependent cross sections, times the appropriate Boltzmann factor:

$$\sigma_L^{(\text{tot})} = \int_0^\infty 2 \left(\frac{E_T}{\pi kT} \right)^{1/2} e^{-E_T/kT} \sigma_L(E_T) dE_T. \quad (11)$$

In Table 2 we give the total cross sections for the four most important processes, at several absolute temperatures: $T = 730 \text{ K}$ and $T = 800 \text{ K}$ are two of the values actually used in heat pipe oven experiments. Other processes, with smaller cross sections, are not considered in the table.

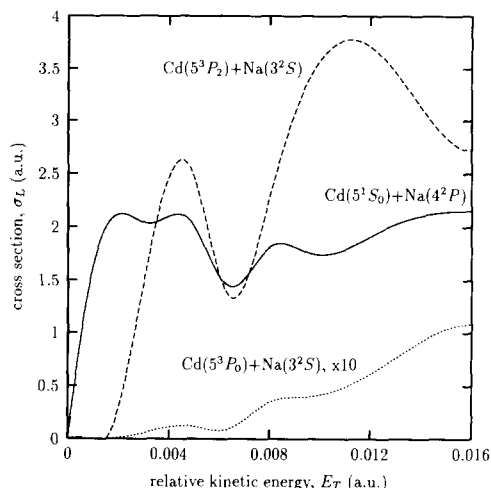


Fig. 4. Cross sections for three anelastic processes involving $\text{Cd}(5^3\text{P}_1) + \text{Na}(3^2\text{S})$, as functions of the relative kinetic energy, E_T .

The result for $\text{Na}(4^2\text{P})$ refers to both components, $4^2\text{P}_{1/2}$ and $4^2\text{P}_{3/2}$, without distinction. The branching ratio depends on the details of the long range potentials, which cannot be accurately reproduced by the ab initio calculations. Theoretically, two limiting cases can be envisaged. The first is an ideally adiabatic behaviour, i. e. no more surface hoppings once the molecule is on the repulsive $^2\Sigma^+$ curve of figure 3; then, only $\text{Na}(4^2\text{P}_{3/2})$ would be produced. In the second case, ideally diabatic, the branching ratio is determined by the projection of the two asymptotic states on the molecular state, $^2\Sigma^+$: then, we should get 1/3 of $\text{Na}(4^2\text{P}_{1/2})$ and 2/3 of $\text{Na}(4^2\text{P}_{3/2})$. Our computed cross sections are closer to the latter prediction.

The cross sections for the intramultiplet relaxation of $\text{Cd}(5^3\text{P}_1)$ should be compared with known experimental data. Total relaxation cross sections for collisions with $\text{Cd}(5^1\text{S})$ are much larger, 596 bohr^2 [15]. Hg is also more effective than Na: $\sigma_L^{(\text{tot})} = 1.7$ and 0.3 bohr^2 for the processes leading to $\text{Cd}(5^3\text{P}_0)$ and to $\text{Cd}(5^3\text{P}_2)$, respectively [16]. Much lower values are found with rare gases [15].

3. Three-body collisions

The results of the trajectory calculations also allow a comparison of the rate of the two-body and three-body

Table 2
Total cross sections at several temperatures

Products	Cross sections $\sigma_L^{(\text{tot})}$ (bohr ²)				
	$T = 690$ K	730 K	765 K	800 K	840 K
$\text{Cd}(5^1\text{S}_0) + \text{Na}(4^2\text{P})$	0.600	0.601	0.602	0.602	0.602
$\text{Cd}(5^1\text{S}_0) + \text{Na}(5^2\text{S})$	0.004	0.004	0.005	0.005	0.006
$\text{Cd}(5^3\text{P}_0) + \text{Na}(3^2\text{S})$	0.025	0.028	0.030	0.032	0.035
$\text{Cd}(5^3\text{P}_2) + \text{Na}(3^2\text{S})$	0.112	0.129	0.143	0.158	0.174

processes (2) and (3), in order to assess their relative importance in the formation of NaCd^* excimers. We have evaluated the steady state density of $\text{Na}+\text{Cd}^*$ collisional complexes. A collisional complex is simply defined as a pair of Cd and Na atoms with a separation smaller than a given threshold, R_0 . A reasonable value for R_0 , probably an upper bound, is $R_0 = 12$ bohr, a distance where even the most attractive potential energy curves have almost reached their asymptotic values. The density of $\text{Na}+\text{Cd}^*$ is equal to the product of the collision rate and of the average lifetime τ :

$$N_{\text{Na}+\text{Cd}^*} = K_S N_{\text{Na}} N_{\text{Cd}^*} \quad (12)$$

and

$$K_S = \left(\frac{8\pi kT}{\mu} \right)^{1/2} B_0^2 \tau. \quad (13)$$

Here μ is the reduced mass and B_0 the arbitrary maximum value of the impact parameter which defines a collision. The lifetime, i.e. the time spent by a pair $\text{Na}+\text{Cd}^*$ at distances smaller than R_0 , depends on R_0 itself, on the impact parameter and on the relative kinetic energy. Averaging with the appropriate Boltzmann factor eliminates the energy dependence. Above a certain impact parameter B_{max} the lifetime vanishes, because the atoms never reach the distance R_0 . If $B_0 > B_{\text{max}}$, averaging over all impact parameters up to B_0 produces a lifetime $\tau(R_0, B_0)$ proportional to B_0^{-2} : in fact, adding more trajectories with large B and vanishing lifetime only changes the total number of trajectories, which is proportional to B_0^2 . Therefore K_S does not depend on the arbitrary parameter B_0 , but only on R_0 . With $R_0 = 12$ bohr, we get $K_S = 4 \times 10^{-22}$ cm³/molecule. The corresponding lifetime, with $B_0 = 15$ bohr, is $\tau = 0.25$ ps.

The complex $\text{Na}+\text{Cd}^*$ can yield a stable excimer NaCd^* by vibrational quenching due to a collision

with a third body M. The rate constant for this process is

$$K_3 = \left(\frac{8kT}{\pi\mu'} \right)^{1/2} \sigma_3. \quad (14)$$

Here μ' is the reduced mass for the pair $(\text{NaCd})-\text{M}$, and σ_3 is the cross section for collisional quenching. The third body M can be identified with the most abundant species in the vapor mixtures produced in heat pipe oven experiments, i.e. Cd. An upper bound for σ_3 is set by assuming that all three-body collisions produce an excimer, rather than dissociating it or quenching it to the ground state. From the atomic radii, we have $\sigma_3 \approx 200$ bohr². In the same way we can evaluate the rate constant of the two-body process (2), involving Na_2 and Cd^* :

$$K_2 = \left(\frac{8kT}{\pi\mu''} \right)^{1/2} \sigma_2, \quad (15)$$

where $\sigma_2 \approx \sigma_3$. The ratio of the three-body versus two-body rate of excimer formation is then

$$\frac{K_S K_3 N_{\text{Na}} N_{\text{Cd}^*} N_{\text{M}}}{K_2 N_{\text{Na}_2} N_{\text{Cd}^*}} \approx 10^{-20} N_{\text{M}}. \quad (16)$$

Here we have made use of the known ratio $N_{\text{Na}}/N_{\text{Na}_2} = 30$ at 800 K. It follows that the rate of the three-body process (3) equates that of (2) only when $N_{\text{M}} \approx 10^{20}$ molecules/cm³, corresponding to a total pressure of about 10 atm. A previous assessment of the rate ratio (16), although based on a similar model, led to a different conclusion [4]: in the absence of an appropriate dynamical treatment, a much higher value for the lifetime of the $\text{Na}+\text{Cd}^*$ collision complex was adopted, thus overestimating the importance of the three-body process. Our low interaction times are due to the fact

that the entrance channel potentials are slightly repulsive, and no transitions to attractive potential curves take place during the collision.

4. Conclusions

The collisions of $\text{Cd}(5^3\text{P}_1)$ with $\text{Na}(3^2\text{S})$ give place to three anelastic processes: energy transfer to Na, with production of $\text{Na}(4^2\text{P})$, or a change in the electronic state of Cd, to 5^3P_0 or 5^3P_2 . The computed cross sections at 800 K are respectively 0.602, 0.032 and 0.158 bohr². The cross sections for other energy transfers, producing lower or higher states of Na, are negligible. Therefore, the observation of emission from $\text{Na}(3^2\text{P}, 3^2\text{D}, 5^2\text{S}$ and $4^2\text{D})$ [8] should be accounted for by invoking other processes, such as radiative decay, collisions with Na_2 , etc. In particular, the strong emission from $\text{Na}(3^2\text{D})$ may be due to the relaxation of $\text{Na}(4^2\text{P})$, by collisions with ground state Na.

We have compared the efficiency of two proposed processes, a two-body collision $\text{Cd}^* + \text{Na}_2$ and a three-body one $\text{Cd}^* + \text{Na} + \text{M}$, in producing NaCd^* excimers: we find that the two-body reaction dominates, and the two rates would be equal only at total pressures about 10 to 100 times larger than usual in heat pipe oven experiments. This conclusion has only a qualitative value, being based on a crude model for the collision processes: more refined predictions would need the knowledge of Cd–Cd–Na potential energy surfaces.

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