

## LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2002 issue.

## NOTES

## The importance of the diabatic channels in the chemi-ionization reaction $O(^3P) + CH(a^4\Sigma^-) \rightarrow HCO^+(X^1\Sigma^+) + e^-$

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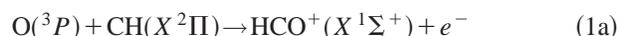
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### I. INTRODUCTION

There is a strong interest<sup>1</sup> in the mechanism of the chemi-ionization reactions



and



Recent MRCI calculations<sup>2</sup> determined a number of intermediate HCO states (*channels*) with low barriers that could allow reactions (1) to occur adiabatically, provided that the total energy of HC+O for a given channel and angle of approach was above the minimum potential energy of HCO<sup>+</sup> at the same angle. This constituted the effective range of angles for the given channel (see Table I of Ref. 2). For reaction (1b) only one adiabatic channel was identified. However, the possibility of a diabatic mechanism for Eq. (1b) presents itself because of an avoided crossing near 4.7 bohr in the C–O coordinate ( $R_{CO}$ ), the only active coordinate in the region of interest. The avoided crossing along  $R_{CO}$  is between the  $2^2\Pi$  and  $1^2\Pi$  states in linear geometry and between the states that correlate to these two upon bending, that is between the  $4^2A'$  and  $3^2A'$  as well as between the  $4^2A''$  and  $3^2A''$  states. It was concluded in Ref. 2 that besides the adiabatic channel, reaction (1b) could proceed via diabatic transitions between the states above through their nonadiabatic couplings in the active coordinate, provided these couplings were strong. That is, provided that the nonadiabatic transition probability (TP) from one to the other of these states is high. Here, we plan to use the nonadiabatic couplings to obtaining an estimate of the TP between the coupled states via an approximate expression and to corroborate the results by employing the qualitative Massey parameter.

### II. NONADIABATIC COUPLINGS

We ran approximate calculations of the nonadiabatic coupling matrix elements  $A(R_{CO})$  between each pair of the coupled states along  $R_{CO}$  keeping the other internal coordinates constant. To estimate the possible effect of orientation, these calculations were done at four angles of approach ( $180^\circ$ ,  $160^\circ$ ,  $140^\circ$ , and  $125^\circ$ ) which were within an effective range as discussed in Ref. 2 and mentioned in Sec. I. The C–H coordinate was kept at 2.12 bohr at all runs. We employed the correlation consistent aug-cc-pVTZ basis set,<sup>3,4</sup> and all energy computations were done at the state averaged multiconfiguration self-consistent field (MCSCF) and MRCI level as implemented in the MOLPRO package.<sup>5</sup> The four electrons in the  $1s$  orbitals of C and O were frozen, and the active space was limited to the nine valence orbitals among which the remaining eleven electrons were distributed. The evaluation of  $A(R_{CO})$  was done by a finite difference procedure using orthogonal orbitals via the DDR and the DIAB programs of MOLPRO.

The main body of calculations was done at the MCSCF level of accuracy at linear and bent geometries in  $C_{2v}(^2\Pi)$  and  $C_s(^2A'$  and  $^2A'')$  symmetries. The validity of the results was tested for a colinear approach against MRCI calculations. The cost of these calculations was excessive (about 460 CPU hours per coupling curve in  $C_s$ ), and it was the reason for not employing them throughout.

### III. TRANSITION PROBABILITY

The quantity of interest here is the single pass TP from the higher to the lower of the coupled states as atom O approaches CH. For relatively accurate probabilities one could solve the semiclassical coupled differential equations for the amplitudes of the involved states. However, a rough estimate of the TP can be obtained by the approximation (in a.u.):<sup>6</sup>

$$P = \sin^2(\pi A_0 \Gamma / 2) \exp(-\Delta E \cdot \Gamma / V_T), \quad (2)$$

where  $A_0$  is the peak of the  $A(R_{CO})$  curve,  $\Gamma$  is the width at half maximum,  $\Delta E$  is the energy gap between the two adia-

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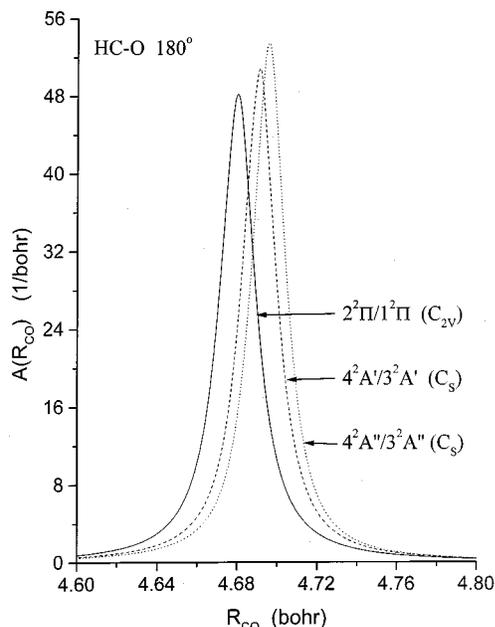


FIG. 1. The nonadiabatic matrix elements between the indicated pairs of states computed at the MRCI level of accuracy for a collinear approach of the HC+O system.

batic states around  $R_{CO}$  and  $V_T$  is the relative velocity between CH and O at temperature  $T$ . In Eq. (2)  $\Delta E$  and  $V_T$  are assumed constant, a condition which is fulfilled here: Within the coupling zone,  $\Delta E$  varies only by about  $\pm 0.0003$  a.u. around the peak, and  $V_T$  corresponds to a relative kinetic energy fixed at 1.5 kT. For the two temperature cases discussed in Ref. 2,  $V_T$  in atomic velocity units (au) is given by  $V_{2000} \approx 0.0012$  au and  $V_{600} \approx 0.00066$  au (1 au =  $2.1877 \times 10^8$  cm/s). A qualitative estimate of the diabaticity of the system is given by the Massey parameter  $\xi(R_{CO}) = V_T \cdot A(R_{CO}) / \Delta E$  (in a.u.). When  $\xi \gg 1$  the system is highly diabatic.<sup>7</sup>

#### IV. RESULTS

Figure 1 depicts the  $A(R_{CO})$  curves for a collinear approach calculated at the MRCI level both in  $C_{2v}(^2\Pi)$  and in

$C_s(^2A'$  and  $^2A'')$  symmetries. The peaks of the graphs are at slightly different locations due to the different configurations entering the corresponding wave functions. However, the coupling strength is about the same in all three calculations as it should be. The corresponding curves at the MCSCF level are not shown, but they are also displaced with respect to each other for the same reason. Table I shows the quantities needed in Eq. (2), as well as the computed TPs at the point of avoided crossing for 2000 and 600 K. In view of the many uncertainties entering the calculation, the comparison of the TPs for the linear approach between the two levels of accuracy justifies the use of the less accurate, but less costly, MCSCF approach we have followed here. Notice that all TPs within a narrow zone around the crossing point, which can be considered as the coupling zone, are of comparable magnitude. Outside this zone  $\Delta E$  changes considerably, and one cannot tell by using Eq. (2) how the TPs vary because Eq. (2) is no longer valid there.

As the angles change from  $180^\circ$  to  $125^\circ$ , the coupling curves are spread over a wider region of the C–O coordinate in such a way that  $A_0$  decreases while  $\Gamma$  increases. These two effects seem to cancel each other, and the TPs remain about the same for all angles of approach within their effective range. It is also apparent that the TPs are rather insensitive to temperature changes. One detail must be cleared up regarding the existence of high barriers after the crossing which would prevent reaction (1b) from taking place. The asymptotic gap between the states 4 and 3 is  $\sim 0.76$  eV.<sup>8</sup> The barrier of the  $3^2A'$  state is lower than this gap at all angles,<sup>2</sup> and reaction (1b) can proceed through this diabatic channel. The barrier of the  $3^2A''$  state is slightly higher than 0.76 eV near linear angles of approach, but it drops quickly below 0.76 eV at smaller angles,<sup>2</sup> and so reaction (1b) can proceed through this diabatic channel as well.

From Table I it seems reasonable to adopt an overall TP of at least 90%, regardless of angle of approach or temperature. As discussed in Ref. 2, however, the effective range of angles does depend on temperature. It was also found that within the coupling zone  $\xi \gg 1$ , a result corroborating the diabaticity of the system. Thus, the diabatic channels are

TABLE I. The peaks  $A_0$  (bohr<sup>-1</sup>) and the widths  $\Gamma$  (bohr) of the coupling curves, the energy gaps  $\Delta E$  (a.u.) of the adiabatic states, and the transition probabilities  $P$  at the avoided crossings. In the  $P$  rows, the first entry refers to 2000 K, and the second to 600 K.

		MRCI		MCSCF		
		180°	180°	160°	140°	125°
$2^2\Pi/1^2\Pi$	$A_0$	49.2	48.2			
	$\Gamma$	0.020 37	0.020 80			
	$\Delta E$	0.000 43	0.000 19			
	$P$	0.99/0.99	0.99/0.99			
$2^2A'/1^2A'$	$A_0$	51.9	57.1	26.0	10.9	6.3
	$\Gamma$	0.019 30	0.017 52	0.038 51	0.091 48	0.156 78
	$\Delta E$	0.000 40	0.000 14	0.000 29	0.000 59	0.000 89
	$P$	0.99/0.99	0.99/0.99	0.99/0.98	0.96/0.92	0.89/0.81
$2^2A''/1^2A''$	$A_0$	55.5	53.4	44.8	28.2	23.4
	$\Gamma$	0.018 04	0.018 77	0.022 28	0.035 57	0.041 69
	$\Delta E$	0.000 41	0.000 17	0.000 16	0.000 24	0.000 29
	$P$	0.99/0.99	0.99/0.99	0.99/0.99	0.99/0.99	0.99/0.98

indeed very important for reaction (1b) and to some extent independent of temperature.

<sup>1</sup>J. M. Dyke, A. M. Shaw, and T. G. Wright, *J. Phys. Chem.* **99**, 14207 (1995), and references therein.

<sup>2</sup>A. Metropoulos and A. Mavridis, *J. Chem. Phys.* **115**, 6946 (2001).

<sup>3</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).

<sup>4</sup>A. K. Wilson, T. V. Maurjk, and T. H. Dunning, Jr., *J. Mol. Struct.:*

*THEOCHEM* **388**, 339 (1997).

<sup>5</sup>MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowls, with contributions from J. Almlöf, R. D. Amos, A. Berning *et al.*

<sup>6</sup>M. Desouter-Lecomte and J. C. Lorquet, *J. Chem. Phys.* **66**, 4006 (1977).

<sup>7</sup>See, for instance, J. C. Tully, *J. Chem. Phys.* **59**, 5122 (1973).

<sup>8</sup>A. Kalemou, A. Mavridis, and A. Metropoulos, *J. Chem. Phys.* **111**, 9536 (1999).