Conditions conducive to the chemi-ionization reaction $O(^3P)+CH(X^2\Pi, a^4\Sigma^-)\rightarrow HCO^+(X^1\Sigma^+)+e^-$
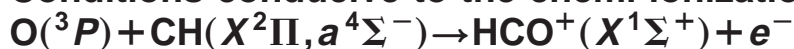
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We have determined the favorable geometries and intermediate HCO states that allow the chemi-ionization reaction $O(^3P)+CH\rightarrow HCO^+(X^1\Sigma^+)+e^-$ to take place in low-energy collisions, when CH is either in the ground $X^2\Pi$ or in the first excited $a^4\Sigma^-$ state. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1405007]

I. INTRODUCTION

There is a strong interest in the mechanism of generation of primary ions during hydrocarbon combustion. The $O+C_2H_2$ reaction pair is of particular interest because both reactants are common intermediates in hydrocarbon flames and because this pair gives a high ion yield per carbon atom.[1] The dominant primary ion generated by this reaction pair, through collisions of its intermediate products O+CH, is the HCO^+ ion.[1,2] It has been usually assumed that only the $X^2\Pi$ ground state of CH contributes to the HCO^+ ion formation

$$O(^3P)+CH(X^2\Pi)\rightarrow HCO^+(X^1\Sigma^+)+e^-. \tag{1a}$$
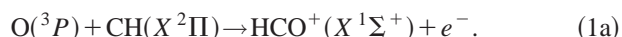
This assumption is in agreement with an old calculation at the INDO level.[3] This calculation had identified reaction (1a) as the main contributor to the ion production. Later, however, it was experimentally determined that reaction (1b) below is also an important contributor to the generation of the HCO^+ ion[4–6]

$$O(^3P)+CH(a^4\Sigma^-)\rightarrow HCO^+(X^1\Sigma^+)+e^-. \tag{1b}$$

The CH($a^4\Sigma^-$) state lies 0.76 eV above the CH($X^2\Pi$) state.[7] Additionally, upon laser excitation of CH to higher excited states, it was found that in such an experiment the ion is generated at a rate which is about 10^3 times higher than the rate of reactions (1) for the 2000–2400 K range of the flames.[8]

More recent *ab initio* calculations at a multireference configuration interaction (MRDCI) level for a collinear O+CH approach[9] concluded that reaction (1a) can occur mainly via the HCO $1^2\Sigma^+$ state because its $1^2\Pi$ state has a barrier of about 0.43 eV while its $^2\Delta$ state goes much higher. Reaction (1b) cannot proceed via the HCO $2^2\Sigma^+$ state because of its large barrier (about 1.6 eV), but it can proceed via the HCO $2^2\Pi$ state through the formation of a diabatic state around its avoided crossing with the $1^2\Pi$ state, provided their interaction is strong.[9] In a subsequent experimen-

tal paper,[10] chemielectron and chemiion spectra were obtained with and without the presence of quenching gases and at various pressures. The authors concluded that HCO^+ is indeed a primary ion in the reaction mixture of oxygen and acetylene and that both reactions (1) are responsible for its generation. They argued that the collinear approach considered in Ref. 9 was not enough for a clear understanding of the ionization mechanism for two reasons: First, the high barrier of the $1^2\Pi$ state may be lowered considerably upon bending, thus opening one more channel to autoionization besides that of the $1^2\Sigma^+$ state. Second, the HCO ($1^2\Sigma^-$) intermediate state correlating adiabatically to CH ($X^2\Pi$) had not been considered in Ref. 9. Since both these arguments are quite valid, we decided to investigate in some detail the geometries and the intermediate HCO electronic states that would enable the reactants O and CH to approach each other sufficiently so that an excited HCO state can in principle be autoionized. The question of whether autoionization will actually occur, given the proper conditions, and to what extend, is left for a future work.

II. METHODOLOGY

In the present work we have used the correlation consistent aug-cc-pVTZ basis set,[11,12] in conjunction with the complete active space self-consistent field (CASSCF)+1+2 multireference CI method (MRCI) employed in the MOLPRO package.[13] The four electrons in the $1s$ orbitals of C and O were frozen. The CASSCF calculations were state averaged, and the active space was limited to the 9 valence orbitals among which the remaining eleven electrons were distributed. In the subsequent MRCI calculations the uncontracted configurations were around 50 million, internally contracted to about one million.

Only calculations between C–O distances of 3 and 6 bohr were done, since our present interest focuses on the region of potentially high barriers. Within this range, the CH interatomic distance was kept constant at 2.12 bohr to avoid costly optimizations. This may have overestimated the barriers by ~0.015 eV and has no effect on our conclusions. All

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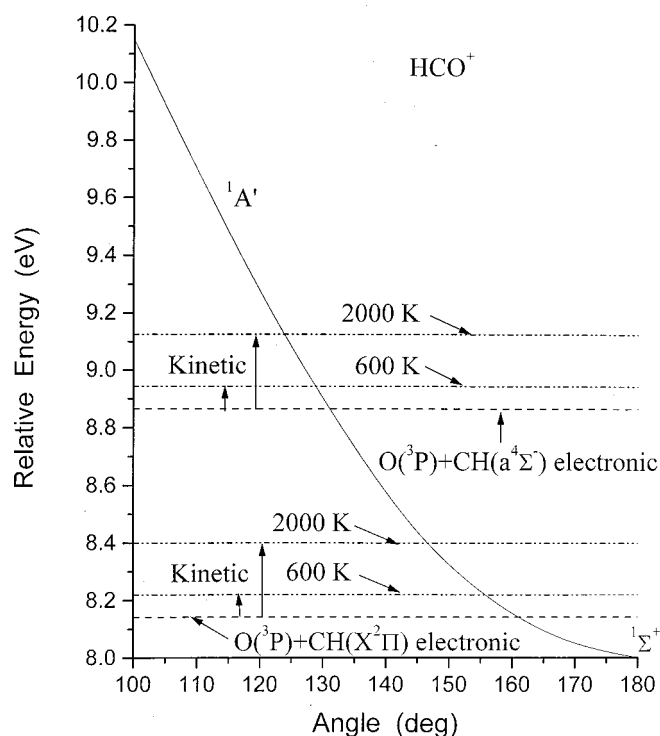[b)]Fax: ++30-1-7274752. Electronic mail: mavridis@chem.uoa.gr

FIG. 1. The optimized energies of the HCO$^+$ cation as a function of the bond angle. The electronic and total asymptotic energies of the reactants are shown for reaction temperatures of 2000 and 600 K. The energy scale is relative to the ground-state minimum of HCO($X\,^2A'$).

FIG. 2. The potential curves for the HCO states arising from the asymptotic O(^3P)+CH($X\,^2\Pi$) and O(^3P)+CH($a\,^4\Sigma^-$) reactants in a linear geometry and calculated in both the C_{2V} (dashed lines) and the C_S (solid lines) point groups. In C_S, only the curves of A' symmetry are shown. The optimized minimum of the HCO$^+$ cation at its linear geometry is also shown. The energy scale is relative to the ground-state minimum of HCO.

energy levels mentioned below are relative to the $X\,^2A'$ global ground-state minimum of HCO, which in our level of accuracy is -113.6917 a.u., and which is located at $R_{CH} = 2.0977$ bohr, $R_{CO} = 2.2366$ bohr and $\theta = 126.41°$. In the HCO$^+$ calculations (in linear and bent geometries), the C–H distance was optimized at the MRCI level, and its linear $X\,^1\Sigma^+$ ground-state minimum was found to be 8.000 eV above the HCO ($X\,^2A'$) minimum.

III. REACTION FEASIBILITY CONSIDERATIONS

At least two conditions must be fulfilled in order for the associative ionization reactions (1) to proceed. One condition is that for every chosen angle of approach the asymptotic electronic energy plus the relative kinetic energy of the reactants at the reaction temperature must be above the minimum (in the C–O coordinate) of the potential energy of the ground ionic state of HCO$^+$ corresponding to this angle. As the ion bends away from its linear minimum and goes into $^1A'$ symmetry, the energy of the new minimum increases and may eventually be shifted to a level higher than the total (electronic plus relative kinetic) asymptotic energy of either the ground or the excited-state reactants. In such a case no ionization can occur via any intermediate HCO state (*channel*) correlating to these reactants, since no resonance can exist between the vibrational levels of HCO and those of its bent ion.

Depending on the reaction temperature and the type of experiment, the relative kinetic energies vary from experiment to experiment and have a distribution within the same experiment. Here, we will consider two representative tem-
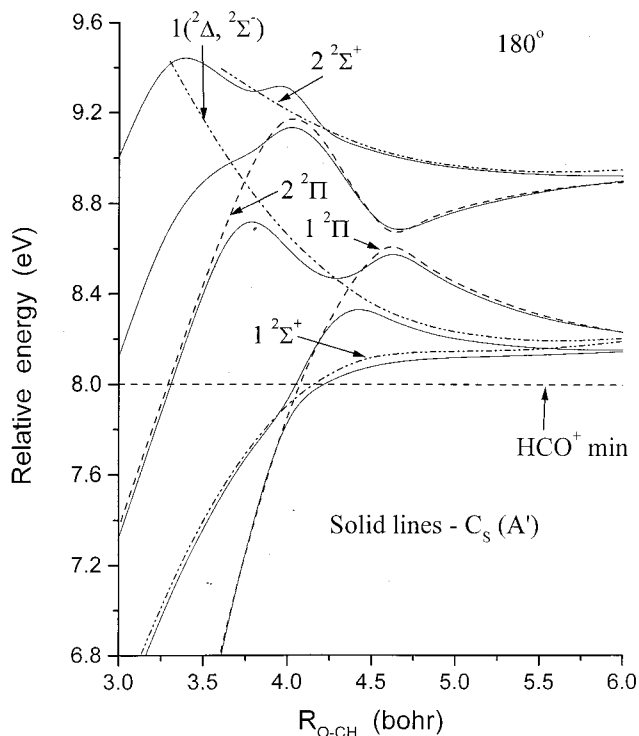
perature limits. In the beam experiments of Ref. 10 the highest temperature is 600 K[14] corresponding to $\sim$0.078 eV in relative kinetic energy, while in the hydrocarbon flame experiments of Ref. 8 the reaction temperature is about 2000 K corresponding to $\sim$0.26 eV. Assuming for now that the CH radical is in its ground vibrational state, the total asymptotic energy limits (electronic plus kinetic) of the ground-state reactants in (1a) vary from 8.142 eV (pure electronic) to 8.220 eV (600 K) to 8.400 eV (2000 K), while the asymptotic energy limits of the excited-state reactants in (1b) vary from 8.865 (pure electronic) to 8.943 eV (600 K) to 9.124 eV (2000 K) (*vide infra*). Figure 1 shows the minimum of the ionic potential energy as a function of the bending angle, as well as the limits of the asymptotic energies of the reactants. Unless a drastic rearrangement to larger angles takes place near the left-hand turning point, it is obvious that at 2000 K the ground-state reactants in (1a) cannot be participants in the autoionization process for angles of approach smaller than 147°; this limit for the excited-state reactants in (1b) is about 124°. The corresponding limits at 600 K are 155° (1a) and 129° (1b). A contributing factor at the high-reaction rates upon excitation of CH[8] could be that the asymptotic energies lie above the ionic minimum for many more angles of approach than in the present case.

Once the first condition is fulfilled, a second condition must be considered. That is, there must be one or more intermediate HCO states (*channels*) with a barrier low enough so that the left-hand side of the potential can be reached as
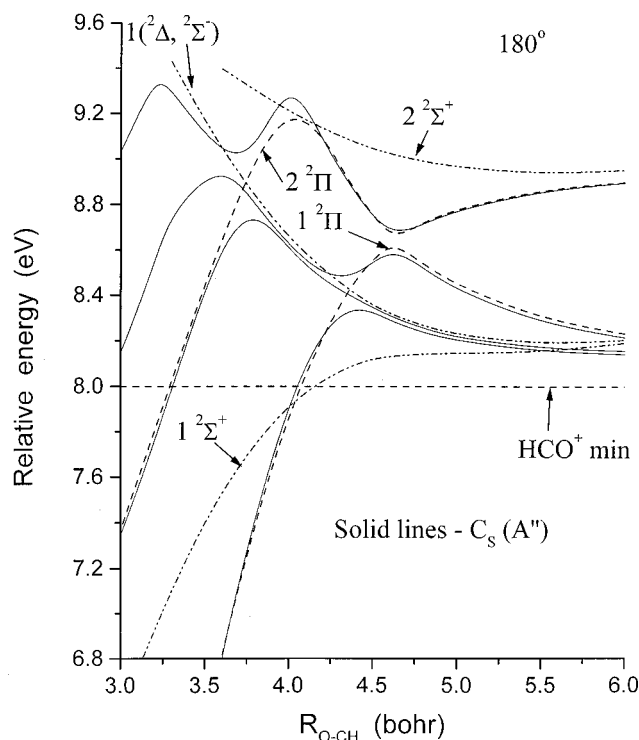
FIG. 3. Same as in Fig. 2, but for the curves of A'' symmetry.

FIG. 4. The potential curves of A' symmetry for the HCO states arising from the asymptotic $O(^3P) + CH(X\,^2\Pi)$ and $O(^3P) + CH(a\,^4\Sigma^-)$ reactants at the indicated angles of approach. The energy scale is relative to the ground state minimum of HCO.

the reactants approach each other at a kinetic energy dictated by the experimental conditions. Here, we assume that for a given channel a barrier of about 0.26 eV for 2000 K or 0.078 eV for 600 K is the highest one that would allow the reaction to proceed through that channel at the corresponding temperature.

IV. RESULTS

In a collinear approach, there are four channels arising from the ground-state reactants in (1a): the $1\,^2\Pi$, the $1\,^2\Sigma^+$, the $1\,^2\Delta$ and the $1\,^2\Sigma^-$; there are two channels arising from the excited state reactants in (1b): The $2\,^2\Pi$ and the $2\,^2\Sigma^+$. The calculations in the linear geometry were done in the C_{2V} point group, which is the next best to $C_{\infty V}$. Considerable insight, however, as to the behavior of the potential curves in a nonlinear approach can be obtained by running the same calculations in the C_S point group while maintaining a linear geometry. So another set of the calculations for a linear geometry were run in the C_S group as well. In C_S the states arising from (1a) are six: three with A' symmetry and three with A'' symmetry; those arising from (1b) are three: Two A' states and one A'' state. The additional states appearing in C_S are due to the fact that the Δ, Π states have components in both the A' and A'' symmetries. Figure 2 depicts the C_{2V} curves with the $C_S(A')$ curves superimposed. Figure 3 depicts the C_{2V} curves with the $C_S(A'')$ curves superimposed. In both Fig. 2 and 3, the $^2\Sigma^-$ and the $^2\Delta$ curves run very close to each other, so we have shown only the $^2\Delta$ curve in order to avoid clutter.

First let us consider the strictly linear channels as candidates for reactions (1). For (1b), the $2\,^2\Sigma^+$ and the $2\,^2\Pi$ states must be excluded because they have high barriers.
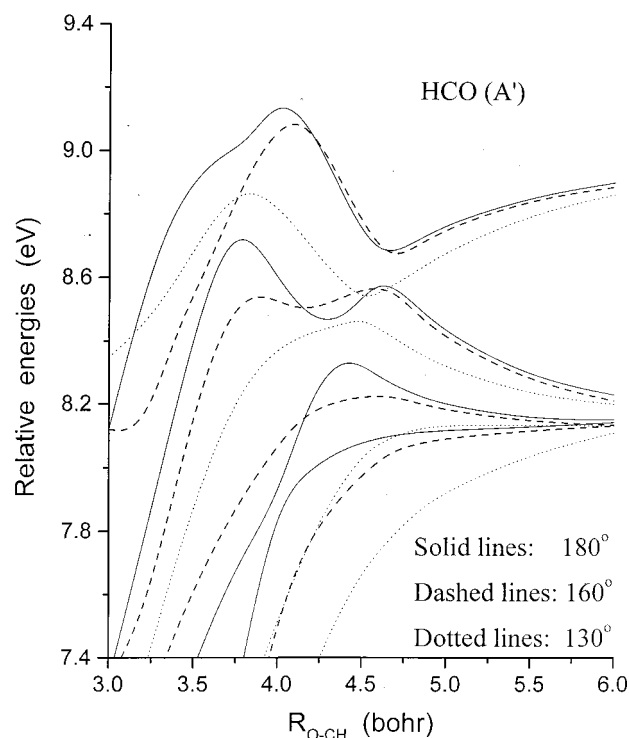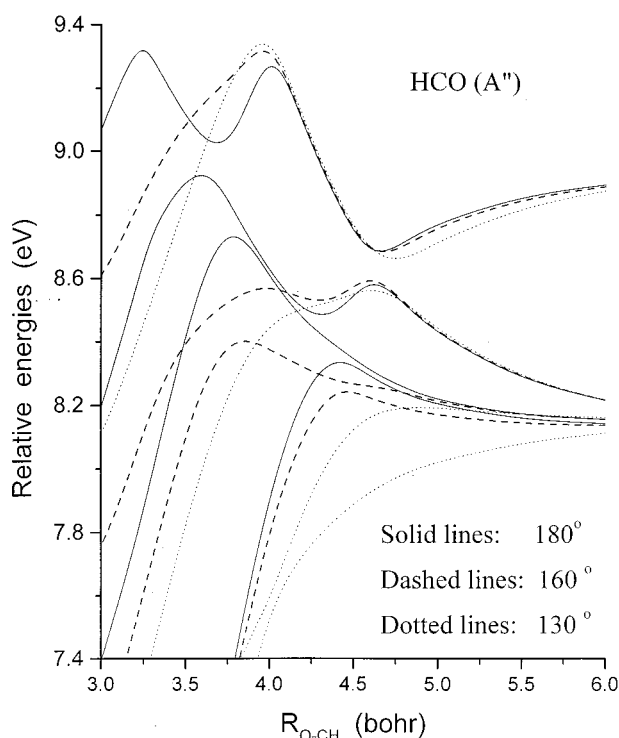
However, the $2\,^2\Pi$ state can affect the chemi-ionization through a *diabatic* transition to the $1\,^2\Pi$ state at the point of their avoided crossing. For (1a), the lowest $1\,^2\Pi$ state must be excluded because it has a barrier of ~0.43 eV; the $1\,^2\Delta$ and the $1\,^2\Sigma^-$ states must also be excluded because they are repulsive. This leaves only the $1\,^2\Sigma^+$ state as a potential channel, which however, in a strictly linear geometry is repulsive in the C–H *coordinate*[15,16] and must also be excluded. Thus, in a strictly linear approach only reaction (1b) seems feasible.

To consider the situation for nonlinear approaches, one can first examine the C_S potential curves shown in Figs. 2 and 3 and then run calculations at smaller angles of approach to observe the trends of the curves. We have chosen the angles of 160° and 130° for this purpose; Figs. 4 and 5 clearly show these trends, which we discuss in detail below. First we consider the reaction at the 2000 K limit. Let us start with the channels pertaining to (1a). The $^2A'$ states exhibit avoided crossings near the points where the $1\,^2\Sigma^+$, the $1\,^2\Pi$ and the $1\,^2\Delta$ states cross, and their character changes considerably as the O–CH distance diminishes. Thus the $1\,^2\Sigma^+$ state ends up as the $X\,^2A'$ state, and the $1\,^2\Pi$ state ends up as the $2\,^2A'$ state. In the C–H *coordinate* the intersection of the $1\,^2\Sigma^+$ and $1\,^2\Pi$ states becomes an avoided crossing of the $X\,^2A'$ and $2\,^2A'$ states thus generating a barrier of about 1.1 eV for the $X\,^2A'$ state. This is clearly shown in Fig. 6, which is a cut through a previously known conical intersection.[17] Therefore, this channel is a candidate for reaction (1a). The A' component of the Δ state ($2\,^2A'$) has a barrier of ~0.20 eV, which becomes ~0.095 eV at 160° and

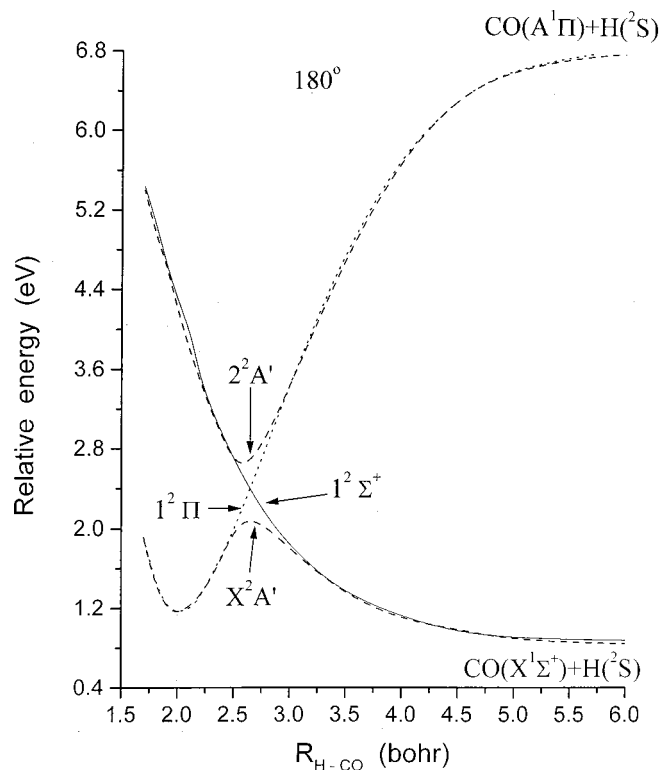FIG. 5. Same as in Fig. 4, but for the curves of A'' symmetry.

FIG. 6. Potential curves in the C–H coordinate for a linear HCO geometry and for a C–O distance of 2.2 bohr. The intersection of the $1\,^2\Sigma^+(^2A_1)$ and $1\,^2\Pi(^2B_2)$ states in C_{2V} symmetry becomes an avoided crossing between the $X\,^2A'$ and $2\,^2A'$ states in C_S symmetry. The energy scale is relative to the ground-state minimum of HCO.

disappears at 130°, and so this component must also be included as a candidate for (1a). In Ref. 10, as mentioned in the Introduction, it was suggested that the barrier of the $1\,^2\Pi$ state could possibly be lowered for lower angles of approach. Unfortunately this barrier remains practically constant for the useful angles of approach (180°–147°) and becomes smaller than 0.26 eV only for angles below 130°. Moreover, the resulting $3\,^2A'$ curve exhibits an avoided crossing at the point of intersection of the $1\,^2\Pi$ and the $1\,^2\Delta$ states and follows the Δ state until its crossing with the $2\,^2\Pi$ state. At this point it forms a "second" higher barrier of about 0.61 eV. At 160°, both extrema form a broad barrier of about 0.40 eV, which diminishes very slowly for smaller angles. So this channel must be excluded as a (1a) candidate. We now consider the A'' states as (1a) candidates. The A'' component of $1\,^2\Pi(3\,^2A'')$ must again be excluded because its barrier goes

from ~0.85 eV near the linear geometry to ~0.49 eV at 160° to ~0.44 eV at 130°. The $2\,^2A''$ state has a barrier of ~0.51 eV around the linear geometry and drops to ~0.29 eV at 160° and to ~0.06 eV at 130°. So this channel is sort of marginal, probably for a narrow range of angles around 150°. The $1\,^2A''$ state has a barrier of ~0.22 eV at the linear arrangement lowered to ~0.13 eV at 160° and disappearing at 130°. Thus, this last channel is the only sure (1a) candidate with A'' symmetry. Turning now to the 600 K limit and using similar reasoning, we are lead to include as (1a) candidates the $1\,^2A'$ and marginally the $2\,^2A'$ state.

Let us now turn to the channels pertaining to the reaction

TABLE I. The estimated barriers of various channels of reactions (1) at three angles of approach and the estimated approximate range of effective angles of approach for all adiabatic channels. Entries with two numbers signify the existence of two consecutive barriers. The barriers may be overestimated by about 0.02 eV or less (see text).

Reaction	States	Channel barriers (eV) at the indicated angles of approach			Estimated effective angle of approach ranges	
		180°	160°	130°	2000 K	600 K
(1a)	$X\,^2A'$	None	None	None	180°–147°	180°–155°
(1a)	$2\,^2A'$	0.22	0.11	None	180°–147°	near 155°?
(1a)	$3\,^2A'$	0.47/0.63	0.47/0.42	0.33	⋯	⋯
(1b)	$4\,^2A'$	0.31	0.24	0.03	160°–124°	145°–124°
(1a)	$1\,^2A''$	0.22	0.13	None	180°–147°	⋯
(1a)	$2\,^2A''$	0.64	0.29	0.06	157°–147°	⋯
(1a)	$3\,^2A''$	0.48/0.85	0.49	0.44	⋯	⋯
(1b)	$4\,^2A''$	0.51/0.51	0.51	0.53	⋯	⋯

(1b). First we note that the $4\,^2A'$ state has a barrier of ~ 0.31 eV around the linear geometry dropping to ~ 0.24 eV at 160° and ~ 0.03 eV at 130°. Therefore, this channel is a (1b) candidate (adiabatically) for both temperatures but for a different range of angles of approach. The same is not true for the $4\,^2A''$ state which maintains a barrier of about 0.5 eV. Table I shows the barriers of the different channels and the estimated angles of approach for each temperature.

Another avenue for the reaction (1b) is the avoided crossing between the $1\,^2\Pi$ and $2\,^2\Pi$ states, which becomes an avoided crossing between the $4\,^2A'$ and $3\,^2A'$ states as well as between the $4\,^2A''$ and $3\,^2A''$ states. The reaction must proceed through the formation of a diabatic state formed at the point of avoided crossing between the adiabatic states 4 and 3, provided the energetics are favorable. The asymptotic gap between the states 4 and 3 is ~ 0.76 eV. Since the barrier of the $3\,^2A'$ state is lower than this gap at all angles, reaction (1b) can proceed through this diabatic channel at all reaction temperatures. Although the barrier of the $3\,^2A''$ state is slightly higher than 0.76 eV at near linear angles of approach, it drops quickly below 0.76 eV at smaller angles, and so the reaction (1b) can proceed through this diabatic channel as well, also at all reaction temperatures.

V. CONCLUSIONS

We have performed *ab initio* calculations on the lowest state of the linear and bent HCO$^+$ cation as well as on the ground and excited states of the linear and bent HCO radical in both C_{2V} and C_S symmetries in an effort to determine which channels and angles of the radical are energetically favorable to the chemi-ionization reactions (1). We have concluded that for reaction (1a) at 2000 K the best angles of approach are between 180° and 147°, and the most probable channels are the $X\,^2A',2\,^2A',1\,^2A''$ and maybe the $2\,^2A''$

states of HCO. At 600 K the best angles are between 180° and 155°, and the most probable channels are the $X\,^2A',2\,^2A'$, and maybe the $1\,^2A''$ states of HCO. For reaction (1b) the best angles of approach are between 180° and 124°, and the most probable channels are the $4\,^2A'$ state (adiabatically) and the $2\,^2\Pi$, $4\,^2A'$, and the $4\,^2A''$ states via diabatic couplings.

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