GETTING CO_2 TO REACT ISN'T EASY: HITTING IT HARD WITH ATOMIC OXYGEN OR WITH HOT ELECTRONS

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Getting CO_2 to react isn't easy. In this work we discuss two approaches to doing this that involve high energy species, and we use computational chemistry methods to reveal what are the possibilities.

In our first study we consider CO_2 in the gas phase, and we collide the molecule with either atomic oxygen or argon. Here the calculations are done using "direct dynamics" in which trajectories are propagated on the ground state Born-Oppenheimer potential energy surface, with CO_2 initially in its zero point state (quasiclassical method) with zero temperature rotations. The potential energy surface is generated on the fly using density functional theory (B3LYP functional with a 6-311G(d) basis). The resulting cross sections are showing in Fig. 1,[1] where we see that the biggest reactive cross section involves exchange of one oxygen with the other (oxygen exchange). This result was presented in an earlier study with a smaller basis,[2] and the results are very similar. What we see is consistent with a modest barrier (about 0.86 eV) leading to a relatively large cross section (several atomic units). New results in the present work include cross sections for oxygen abstraction and insertion-elimination in which O' + CO_2 gives CO + OO', and O_2 + CO', respectively. These reactions have a higher barrier (2.48 eV and 3.52 eV, respectively) and the cross sections are down by a factor of 10 from the exchange cross section even at energies well above the barrier. Note that

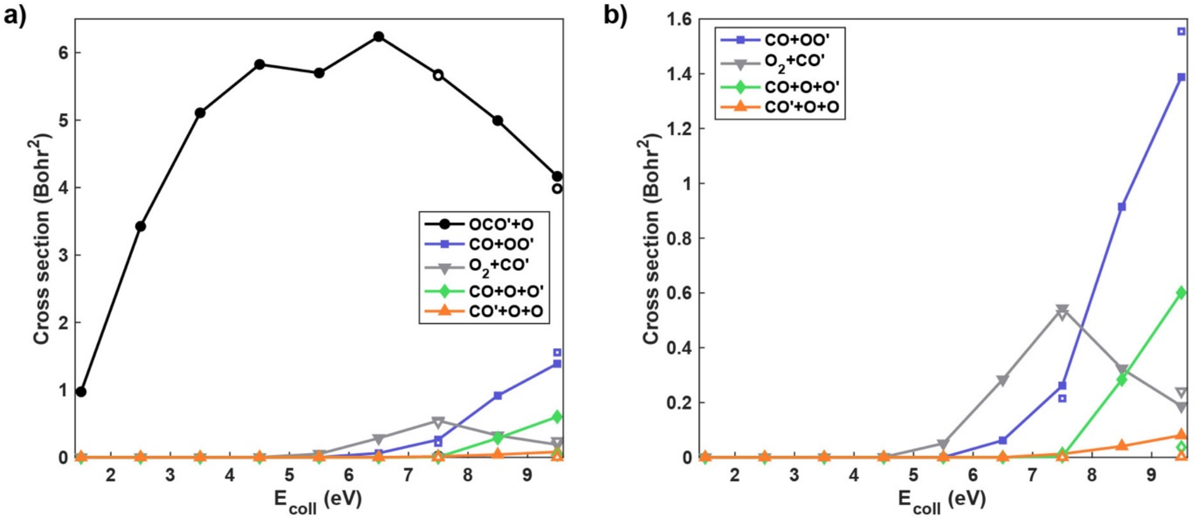

Figure 1. (a) Reaction cross sections at collision energies from 1.5 to 9.5 eV. **(b)** Zoomed cross sections at collision energies greater than 5.5 eV. The reaction cross sections are separately calculated for oxygen exchange (COO' + O, reaction (1), black), single oxygen abstraction (CO + OO', reaction (2), purple), insertion-elimination (CO' + OO, reaction (3), gray), single oxygen dissociation (CO + O + O', reaction (4), green), and insertion-dissociation (CO' + 2O, reaction (5), orange). The open labels at a collision

energy of 7.5 eV and 9.5 eV are the cross sections calculated after considering the intersystem crossing to the quintet surface.

the insertion-elimination process has a lower threshold than abstraction in spite of the higher barrier, which is an interesting dynamical effect. Also, in the figure we see that there is a finite cross section for dissociation at collision energies above 7.5 eV to give CO + O + O', corresponding to collision induced dissociation (CID). Further, we see a cross section for CO' + O + O that is smaller than for CO + O + O'.

The BOMD calculations used to generate these cross sections are concerned with dynamics on the lowest triplet potential surface (the ground state of the reactants) and therefore do not account for intersystem crossing (ISC). However, the dissociation product with the lowest energy is $CO(^1\Sigma_g^+) + 2O(^3P)$ where singlet, triplet and quintet surfaces are possible. Only the lowest triplet correlates to the surface used in our ground state triplet BOMD studies, however we find that none of our $O(^3P) + CO_2$ trajectories produce $CO(^1\Sigma_g^+) + 2O(^3P)$ as products. In an effort to investigate the effect of nonadiabatic processes involving the singlet and quintet surfaces, we performed QCT calculations that include trajectory surface-hopping (TSH) at collision energies of 7.5 and 9.5 eV (Table 1). In these calculations, we required that ISC only occurs the first time when the triplet surface crosses with the singlet or the quintet surface so the results should be an upper bound to ISC probabilities. Since the hopping probability is very small (0.2% ~ 2%), the ISC contribution to the cross sections is always small (especially for the singlet final state) at energies below 7.5 eV. However, at energies of 7.5 eV and above, ISC to give the quintet state becomes important. At E_{coll} = 7.5 eV, 11.2% of the trajectories undergo surface hopping from the triplet surface to the quintet surface. In spite of this the change in overall exchange cross section is small (the value decreases slightly in Table 1). However, hopping in combination with abstraction or dissociation has a high enough probability such that the total cross sections for abstraction change (decrease) by as much as 20% compared to the BOMD results, and the cross sections for dissociation, which are very small, change (increase) by factors of four or more. The changes at 9.5 eV are even more significant. Overall the dissociation cross sections in this study are small enough that further refinement of these results is not justified. However these results refer to CO_2 initially in its ground vibrational state (appropriate to low temperature). We have seen in studies of Ar + CO_2 (unpublished) that under the high temperature conditions of hypersonic ablation, the CO_2 can be highly vibrationally excited, and this leads to significant dissociation cross sections (much higher

Table 1. ISC cross sections for the five reaction pathways. Unit: a_0^2.

	7.5 eV No ISC	7.5 eV Triplet–Quintet*	7.5 eV Triplet–Singlet**	9.5 eV No ISC	9.5 eV Triplet–Quintet*
OCO'+O	5.679	5.659	0.019	4.166	3.984
CO+OO'	0.261	0.215	0.011	1.388	1.555
CO'+OO	0.544	0.523	0.004	0.187	0.241
CO+O+O'	0.003	0.012	0.000	0.601	0.037
CO'+O+O	0.012	4.7E-04	0.000	0.080	0.002

* This calculation includes intersystem crossing: the trajectories are required to hop from the triplet potential energy surface to the quintet surface at the first time when these two surfaces cross.

** This calculation includes intersystem crossing: the trajectories are required to hop from the triplet potential energy surface to the singlet surface at the first time when these two surfaces cross.

than those in Table 1). This suggests that if we are interested in conditions leading to a high cross section for dissociation in O + CO_2 collisions, it will be important to consider CO_2 that is highly vibrationally excited.

Another way to make CO_2 react is by adding or subtracting electrons, as a result of photoexcitation when the CO_2 is in contact with a gold nanocluster (or nanoparticle). This process is especially efficient when the gold cluster is excited at a wavelength where plasmon excitation can occur, leading to what is called plasmon-driven chemistry. This is a complex process, as plasmons are collective excitations of conduction electrons in metals and other materials, and the excitation needs to be followed by a dephasing before electron or hole transfer can take place that can lead to reaction. In the past few years the Schatz group has been involved in several attempts to develop a dynamics theory that describes this process[3,4], particularly for the dissociation of H_2 on gold clusters. If the cluster is small enough, say 6 atoms, the excitations are not plasmonic, and traditional methods for describing the excited state potential surface and the nonadiabatic dynamics that leads to to electron transfer can be used.[4] For larger clusters, say a few hundred atoms, a method was developed based on the Ehrenfest approximation that averages over the many states that can be excited in plasmon excitation.[3] Doing this in the context of density functional theory is computationally intensive, so the past work has involved severe approximations including treating the dynamics by a jellium model and using ultrashort very intense pulses. Recently a new opportunity has arisen that is described in this abstract based on the DFTB+ electronic structure model. This is a tight binding (semiempirical) code that now has the capability of doing real-time TDDFT (RT-TDDFT) calculations in the Ehrenfest approximation, and including for nonadiabatic effects. In this study we will use this method to study absorption spectra and plasmon-driven electron transfer leading to CO_2 dissociation.

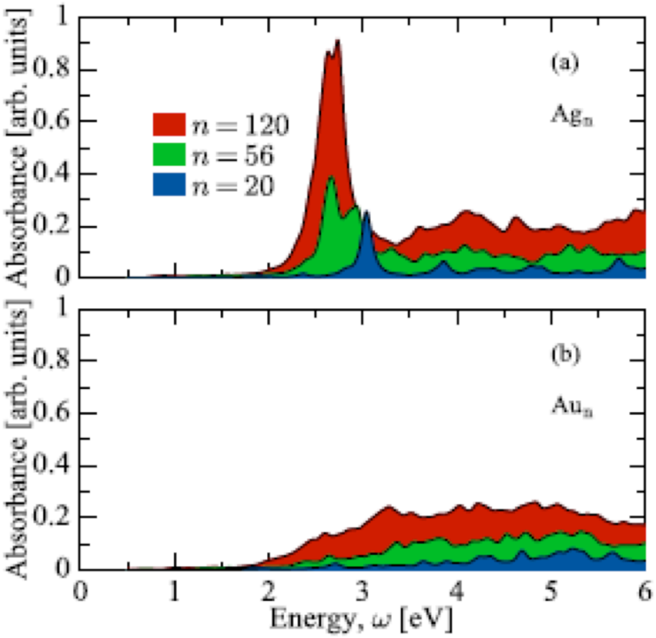

Figure 3. Spectra of tetrahedral silver (top) and gold (bottom) clusters, as obtained from DFTB+ for clusters with 20, 56 and 120 atoms.

The results we have generated with DFTB+ are presented in Figures 3 and 4. In Fig. 3, we show spectra for several silver and gold clusters, all assumed to be tetrahedral in shape, with atom numbers of 20, 56 and 120. The spectra show results that are in excellent agreement with results obtained long ago using a conventional TDDFT calculations, but the present calculations are done in minutes rather than days. For the Ag clusters there is a sharp plasmon resonance at about 2.5 eV, while for the Au clusters the plasmonic character is much weaker, with peaks near 2.5 eV that will turn into stronger plasmons for larger cluster sizes.

In Fig. 4 we show the results of RT-TDDFT calculations in which a CO_2 molecule is placed at the tip of the tetrahedral clusters and then hit with a 25 fs pulse of light that is centered at 2.75 eV energy (close to the plasmon). The gaussian pulse profile is shown in the top panel. The other panels show the probability of dissociating the CO_2 (breaking either one C-O ($p_d^{(1)}$) or two C-Os ($p_d^{(2)}$) or none ($p_d^{(0)}$)) as a function of time, with the probability determined by averaging over the CO_2 vibrational phases (quasiclassical treatment). The results refer to 56 and 120 atom clusters, and we see that after about 30 fs there is considerable probability for dissociation, especially for the 120 atom cluster. A detailed analysis of the results (not shown) shows that dissociation is induced by transfer of charge to the CO_2 while the pulse is on. This temporarily excites the CO_2 to repulsive states (similar to what we learned about H_2 dissociation in our jellium model study, but here with much longer pulses (25 fs instead of 2 fs) and lower intensities (1 V/Angstrom). This provides a detailed model for the plasmon-driven process that we plan to use more generally to study many chemical reactions in future studies.

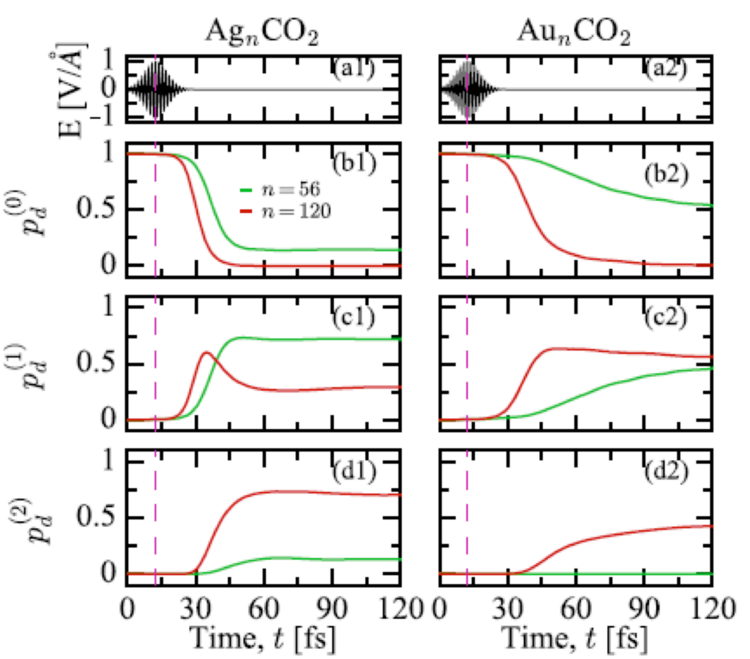

Figure 4. Dissociation probabilities as defined in the text for the dissociation of a CO_2 molecule at the tip of tetrahedral silver and gold clusters, as a function of time in the presence of a 25 fs light pulse at 2.75 eV (pictured in the top panel).

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