## Chemical reaction dynamics when the Born–Oppenheimer approximation fails

# Understanding which changes in the electronic wavefunction might be restricted

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Whether a reaction is occurring in the gas phase or condensed phase, electronically nonadiabatic effects can become important if the adiabatic reaction coordinate requires a considerable change in the electronic wavefunction. The experiments and analysis presented here seek to make progress on a difficult and important problem, that of developing a back-ofthe-envelope method to predict which energetically allowed products are favoured or disfavoured when significant electronic configuration changes are required to access one or all of the possible product channels. By examining the off-diagonal matrix elements responsible for coupling electronic configurations in the initially excited molecule with those of the products, we begin to formulate a hierarchy of what electronic configurations are strongly vs. weakly coupled. Hence, the paper focusses on understanding how an electronic wavefunction is most likely to change during a chemical reaction when it cannot adjust adiabatically during the nuclear dynamics.

We begin by analyzing the results of two prior series of experiments in order to develop a hierarchy of propensity rules for electronic configuration changes from reactant to products. Analysis of experimental and computational results on the competition between C-Br fission and C-Cl fission in  $n_0 \pi^*_{C=0}$  excited Br(CH<sub>2</sub>)<sub>2</sub>COCl and on the  $\pi\pi^*$  photofragmentation channels of nitric acid suggest the following. If the one-electron configuration interaction matrix elements between the reactant electronic configuration and a product electronic configuration are zero, then the reaction is strongly susceptible to nonadiabatic suppression of the reaction rate and/or appearance of nonadiabatic asymptotic products. One must then analyze the remaining two-electron configuration interaction (Förster- and Dexter-type) matrix elements. If the two-electron change required to couple the reactant and product electronic configurations involves simultaneous configuration changes on two spatially/electronically isolated functional groups, then that product channel is strongly disfavoured. We show why this is the case by examining the two-electron integrals for C-Br fission in Br(CH<sub>2</sub>)<sub>2</sub>COCl and for the forbidden NO<sub>2</sub>(1<sup>2</sup>B<sub>1</sub>) + OH(A'') channel from  $\pi\pi^*$  excited nitric acid, comparing them to those for the  $NO_2(1^2B_2) + OH(A')$  channel where the orbitals involved are localized on the same functional moiety. This hierarchy in electronic coupling motivates the introduction of a 'restricted adiabatic' correlation diagram to predict which product channels are electronically accessible.

In the final section of this paper we present new results on the photodissociation of N,N-dimethylformamide following  $\pi_{nb}\pi^*$  excitation at 193 nm, where we test the ideas developed from analysis of the previous work. Our measurement of the photofragment velocity and angular distributions

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of the dissociation products reveals that dissociation pathway to form HCO  $+ N(CH_3)_2$  results in formation of  $HCO(\tilde{X}) + N(CH_3)_2(\tilde{A})$  but not  $HCO(\tilde{A}) + N(CH_3)_2(\tilde{X})$ . As both are energetically allowed product channels in the singlet A' manifold, the selectivity may be analyzed with respect to the required change in electronic configuration to access each asymptotic product channel. To understand the experimental results in the context of the model developed from the prior work, we consider both one-electron and two-electron contributions to the configuration interaction matrix elements between the reactant and product electronic configurations to determine which product channels are most likely to be accessed.

## 1 Introduction

Whether a chemical reaction, gas or condensed phase, is initiated in the ground electronic state or an excited electronic state, electronic nonadiabaticity can strongly influence the reaction dynamics.<sup>1</sup> Electronic nonadiabaticity can be simply understood as the inability of the electronic wavefunction to readjust on the time scale of the nuclear dynamics to the changing adiabatic electronic wavefunction along the Born-Oppenheimer<sup>2</sup> potential energy surface for the reaction. (The nature of the adiabatic electronic wavefunction at each point along that potential surface is calculated, with the geometry of the nuclei fixed, by diagonalizing the electronic part of the Schrödinger equation.) The ability of a system to follow an adiabatic pathway to dissociation depends on the electronic rearrangements necessary as the nuclei separate. In particular, in extended molecular systems in the gas phase or, even more commonly, in the condensed phase, the spatial separation and orientation of electronic orbitals potentially involved in the reaction can substantially alter the importance of electronic nonadiabaticity. One may rigorously include the effects of nonadiabatic dynamics by including the neglected terms,<sup>3,4</sup> such as internuclear coordinate derivative coupling of the adiabatic electronic eigenfunctions, in the Hamiltonian for the nuclear Schrödinger equation, but this is often a daunting calculation for even simple systems like nitric acid or amide photodissociation. We propose instead to begin to develop a crude qualitative understanding, based on considering the configuration interaction between reactant and product electronic configurations, of a molecular system's ability to access one or more energetically allowed reaction channels, whether adiabatic or nonadiabatic.

When adiabatic reaction channels compete, we are used to the luxury of being able to compare the relative barrier heights and preexponential factors of the energetically allowed reaction channels to get a good estimate of which reaction products will dominate.<sup>5,6</sup> However, when nonadiabatic reaction channels compete with each other or with adiabatic ones, or when nonadiabatic recrossing<sup>7</sup> affects the competition between adiabatic reaction channels, we must not only consider the nuclear dynamics, but also the probable changes in electronic wavefunction. In this paper, we examine the coupling between the reactant electronic configuration(s) and the possible product electronic configurations in order to better understand what influences the ability of the electronic wavefunction to change character. We examine three different classes of photodissociation reactions, each of which involves a change in the character of the electronic wavefunction leading to the observed product channels. By looking at the coupling between the initial and final configurations, we can learn about what factors mediate the choice of the electronic wavefunction among energetically accessible reaction pathways. These three classes of reactions suggest a hierarchy of configuration interaction matrix elements which allow one better to predict the probable reaction pathways, both adiabatic and nonadiabatic, in molecular systems.

We begin by reviewing previous experimental and computational results on the competition between C-Br fission and C-Cl fission in  $n_0 \pi^*_{C=0}$  excited Br(CH<sub>2</sub>)<sub>2</sub>COCl and on the  $\pi\pi^*$  photofragmentation channels of nitric acid. The analysis of these results suggests a hierarchy in the configuration interaction matrix elements that couple the reactant electronic configuration to the possible product configurations. We then test the proposed model for identifying the most probable electronic changes in a new study, that of the photodissociation of N,N-dimethylformamide at 193 nm.

## 2 Coupling between electronic configurations: distinguishing between twoelectron matrix elements involving one *vs*. two functional moieties

This section reviews two previous studies of the branching between product channels which are energetically allowed but difficult to access electronically. This difficulty arises because the one-electron configuration interaction matrix elements are zero, so the coupling between reactant and product electronic configurations relies on two-electron matrix elements. Reactions in which individual orbital symmetry is not conserved along the reaction coordinate, Woodward-Hoffmann forbidden reactions,<sup>8</sup> belong to such a category, and recent work has shown that the remaining two-electron matrix elements that couple the reactant and product electronic configurations can be so small that these reactions are particularly susceptible to electronically nonadiabatic suppression of the reaction rate.<sup>9</sup> This section extends that earlier work by comparing product channels which rely on two-electron configuration interaction matrix elements, and contrasting those reactions that require changes in electronic character localized on one functional group with those that require simultaneous electronic changes on two spatially/ electronically isolated functional groups. We propose that the latter product channels, even though energetically allowed, are electronically inaccessible. We introduce a 'restricted adiabatic' correlation diagram to show what product channels are electronically accessible, disallowing correlation to product channels requiring simultaneous configuration changes on two spatially/electronically isolated functional groups.

## 2.1 Spatial dependence of the electron configuration interaction matrix elements in Br(CH<sub>2</sub>)<sub>n</sub>COCl photodissociation

To understand how two-electron configuration interaction matrix elements can depend on the spatial separation of orbitals involved, we first review previous work on the competition between C-Br fission and C-Cl fission in the photodissociation of bromoacetyl chloride (BrCH<sub>2</sub>COCl)<sup>10</sup> and bromopropionyl chloride [Br(CH<sub>2</sub>)<sub>2</sub>COCl]<sup>7</sup> following  $n_0 \pi^*_{C=0}$  excitation at 248 nm. Excitation of Br(CH<sub>2</sub>), COCl to the lowest <sup>1</sup>A" potential energy surface did not result in domination of the low barrier C-Br fission channel over the higher barrier C-Cl fission channel, as would have been predicted by statistical transition state theories on a single adiabatic potential energy surface. Instead, the experiments showed that the expected rate of C–Br fission was dramatically reduced in bromoacetyl chloride<sup>10</sup> (C–Br:C–Cl  $\approx$  0.4:1) and effectively completely suppressed in bromopropionyl chloride<sup>7</sup> (C–Br:C–Cl < 0.05:1 from excitation to the  $^{1}A''$  surface) by nonadiabatic recrossing of the C-Br fission reaction barrier. Our complementary *ab initio* calculations<sup>7</sup> confirmed the experimental conclusions, showing that the avoided electronic curve crossing which forms the barrier to C-Br fission is so narrowly avoided, with an energetic separation between adiabats on the order of only 20  $cm^{-1}$ , that over 99.9% of the trajectories<sup>9</sup> attempting to cross the barrier to C-Br fission instead retain their initial  $n_0\pi^*(C=O)$  character and hop to the bound region of the upper adiabat, suppressing the rate constant for C-Br fission by orders of magnitude in bromopropionyl chloride. The experiments made it clear that when the adiabatic approximation fails, it can substantially reduce the rate constant for a chemical reaction.

Let us now examine the configuration interaction matrix elements that couple the reactant and product electronic wavefunctions in bromopropionyl chloride to better

understand why C-Br fission, though energetically allowed and the channel with the lower barrier height, was, by virtue of the required change in electronic configuration, virtually electronically inaccessible. For the planar conformer of the molecule, the dominant electronic configuration contributing to the electronic wavefunction,  $\Psi_{\rm R}$ , on the reactant side of the barrier is represented by excitation of one electron from the a' no orbital into the a"  $\pi^*_{C=0}$  orbital, while the dominant configuration contributing to the electronic wavefunction,  $\Psi_P$ , on the product side of the barrier is represented by an excitation of one electron from the a"  $np_{Br}$  orbital into the  $\sigma^*_{C-Br}$  orbital. The reactant configuration,  $\{\cdots (np_{Br})^2 (n_0)^1 (\pi^*_{C=0})^1 (\sigma^*_{C-Br})^0\}$ , differs from that on the product side of the barrier,  $\{\cdots (np_{Br})^1 (n_0)^2 (\pi^*_{C=0})^0 (\sigma^*_{C-Br})^1\}$ , by the occupation of four orbitals Because of the symmetries of the orbitals, no one-electron matrix elements can couple the reactant and product electronic configurations:  $\langle n_0 | H | np_{Br} \rangle = \langle a' | H | a'' \rangle = 0$  and  $\langle \pi^*_{C=0} | H | \sigma^*_{C-Br} \rangle = \langle a'' | H | a' \rangle = 0.$  (One can see this in another way by constructing an orthogonal basis for the electronic structure problem. Here, the resulting orbitals in the orthogonal basis look localized as they did in the natural orbital description alluded to above.) In this simplified two-state model, with no orthogonality assumed between reactant and product molecular orbitals or between  $\Psi_{\rm R}$  and  $\Psi_{\rm P}$ , the one-electron resonance/exchange integrals contributing to coupling between the reactant and product electronic configurations are zero due to symmetry, leaving only two-electron integrals to couple the reactant and product electronic configurations at the avoided crossing. For singlet states, the two-electron configuration interaction matrix elements are<sup>11a</sup>

$$V_{12} = 2 \langle \mathbf{n}_{0}(1)\mathbf{n}_{Br}(2) \left| \frac{e^{2}}{r_{12}} \right| \pi^{*}_{C=0}(1)\sigma^{*}_{C-Br}(2) \rangle - \langle \mathbf{n}_{0}(1)\pi^{*}_{C=0}(2) \left| \frac{e^{2}}{r_{12}} \right| \mathbf{n}_{Br}(1)\sigma^{*}_{C-Br}(2) \rangle$$
(1)

When this configuration interaction is small, the electronic wavefunction cannot adjust to the product configuration as the molecule attempts to traverse the reaction barrier, and nonadiabatic recrossing<sup>1,8</sup> effectively suppresses the reaction rate.

It is easy to see why  $V_{12}$  is small in bromopropionyl chloride. The first matrix element in eqn. (1) is analogous to transition dipole-transition dipole (Förster) coupling, depicted schematically in the top frame of Fig. 1, and it decreases with the separation between chromophores. The second matrix element, the Dexter energy transfer mechanism depicted in the bottom frame of Fig. 1, decreases roughly exponentially as the overlap densities  $n_0(1)n_{Br}(1)$  and  $\pi^*_{C=0}(2)\sigma^*_{C-Br}(2)$  decrease. It can be viewed as the simultaneous transfer of an electron from  $n_{Br}$  to  $n_0$  and from  $\pi^*_{C=0}$  to  $\sigma^*_{C-Br}$ . Because the C-Br functional moiety is spatially separated from the C=O moiety, the overlap density  $n_0(1)n_{Br}(1)$  and the overlap density  $\pi^*_{C=0}(2)\sigma^*_{C-Br}(2)$  are both very small at all  $r_1$  and  $r_2$ . Thus, this matrix element is small when the configuration change from reactant to product involves simultaneous changes in the electronic configuration on two spatially separated functional groups. We shall see in the next section that if the configuration changes required are localized on a single functional group, then this matrix element is not as small and the reaction channel becomes accessible (though still difficult, *i.e.*, subject to some electronic nonadiabaticity).

#### 2.2 OH + NO<sub>2</sub> product channels in the 193 nm photodissociation of nitric acid: twoelectron matrix elements involving one vs. two functional moieties

The  $OH + NO_2$  product channels arising from the 193 nm photodissociation of nitric acid<sup>12</sup> reviewed in this subsection demonstrate the qualitative difference between electronic configuration changes on the initially excited portion of the molecule *versus* ones requiring configuration changes on both the initially excited moiety and on another functional moiety not involved in the initial excitation. The experimental results suggest



Fig. 1 Schematic diagram showing the orbitals contributing to Förster and Dexter matrix elements in  $V_{12}$ , responsible for coupling the electronic configurations involved in adiabatic C-Br bond fission following  $n_0 \pi^*_{C=0}$  excitation in Br(CH<sub>2</sub>)<sub>n</sub>COCl. These are labelled both by their character in Br(CH<sub>2</sub>)<sub>n</sub>COCl and by their symmetry with respect to the molecular plane. The relative importance of these two terms is discussed in the text.

a hierarchy of electronic configuration couplings, which allow us to exclude energetically allowed product channels that are electronically inaccessible, representing in a 'restricted' correlation diagram the more likely product channels. Reaction channels which change individual orbital symmetries are hard enough for the electronic wavefunction to follow, but following reaction paths that require orbital symmetries to change on two electronically isolated functional groups is virtually impossible. The potential significance to chemical reactions in gas- or condensed-phase molecules with spatially separated functional groups is clear.

Although it has long been known that both formation of  $OH + NO_2$  and formation of O + HONO occurred in the 193 nm photodissociation of nitric acid,<sup>13-19</sup> recent work<sup>12</sup> shows that both processes exhibit two competing mechanisms, one adiabatic and one nonadiabatic channel. A photofragment time-of-flight spectrum showing the competing channels is shown in Fig. 2; the corresponding product recoil kinetic energy distributions derived from the forward convolution fit of the two  $NO_2 + OH$  channels are shown in Fig. 3. A simple Franck–Condon analysis, described in ref. 12, allows one to assign the higher kinetic energy channel to formation of the adiabatic asymptotic products on the initially prepared 2<sup>1</sup>A' surface,<sup>20</sup> OH + NO<sub>2</sub>(1<sup>2</sup>B<sub>2</sub>), but clearly shows that the second channel is neither of the energetically proximate A' asymptotes, neither OH + NO<sub>2</sub> (1<sup>2</sup>B<sub>1</sub>) nor OH + NO<sub>2</sub> (1<sup>2</sup>A<sub>2</sub>). This section analyzes the configuration interaction matrix elements necessary to access each of these channels, the one observed experimentally and the two by the dissociating molecule, to understand why the competing nonadiabatic channel was neither of these energetically proximate ones.

Excitation of nitric acid at 193 nm accesses the  $2^{1}A'$  potential energy surface via a  $\pi_{nb, 0} \rightarrow 2\pi^{*}_{NO_{2}}$  transition localized on the NO<sub>2</sub> group. The  $2^{1}A'$  surface correlates adiabatically to OH + NO<sub>2</sub> ( $1^{2}B_{2}$ ) at bent NO<sub>2</sub> geometries (see Fig. 4),<sup>20</sup> but this  $1^{2}B_{2}$ 



**Fig. 2** OH<sup>+</sup> time-of-flight data, recorded following nitric acid photodissociation at 193 nm, with a  $10^{\circ}$  source angle with respect to the detector axis. The signal at early arrival times is attributed to fission of the N-OH bond, leading to NO<sub>2</sub> + OH products. Adapted with permission from Fig. 1 of ref. 12.

electronic state of NO<sub>2</sub> does not have the same  $\pi_{nb, 0} \pi^*_{NO_2}$  character as the 2<sup>1</sup>A' state of nitric acid in the Franck–Condon region. Thus, along the N-OH adiabatic fission coordinate the electronic character at the NO<sub>2</sub> group must change in character, resulting in a barrier to dissociation along this adiabat. The dominant electronic configuration contributing to the electronic wavefunction,  $\Psi_R$ , in the Franck–Condon region is represented by excitation of one electron from the  $3a''\pi_{nb,0}$  orbital of nitric acid into the  $4a''\pi^*_{NO_2}$  orbital (see the molecular orbital correlation diagram in Fig. 5), while the dominant configuration contributing to the electronic wavefunction,  $\Psi_P$ , on the product



Fig. 3 Recoil kinetic energy distribution showing the probability of translational energy,  $E_{\rm T}$ , being disposed into the OH + NO<sub>2</sub> reaction products. There are two translational energy distributions for this channel, one of which is shown to be the adiabatic channel leading to OH + NO<sub>2</sub> (1<sup>2</sup>B<sub>2</sub>). The other channel is as yet unassigned. The labels (1<sup>2</sup>B<sub>2</sub>, *etc.*) show the maximum available energy for recoil kinetic energy (higher  $E_{\rm T}$ ) and the most probable recoil kinetic energy (lower  $E_{\rm T}$ ) for formation of various NO<sub>2</sub> product states, with energies obtained from a Franck–Condon projection at the NO<sub>2</sub> geometry in nitric acid. Adapted with permission from Fig. 7 of ref. 12.



Fig. 4 Fully adiabatic correlation diagram for the dissociation of nitric acid to  $OH + NO_2$  at bent  $NO_2$  geometries. The vertical excitation energies for the nitric acid states are taken from ref. 21, and the  $NO_2$  energies are taken from ref. 22 using the vertical excited state energy of  $NO_2$  at the  $NO_2$  geometry in nitric acid. Solid lines indicate states of A' symmetry and dashed lines indicate states of A'' symmetry with respect to the nitric acid molecular plane. Adapted with permission from Fig. 11 of ref. 12.

side of the barrier is represented by a valence bond configuration of  ${}^{1}n_{20} \sigma^{*}{}_{N-OH}$  character corresponding to excitation from the ground state configuration of an electron from the 9a'  $n_{20}$  orbital into the 10a'  $\sigma^{*}{}_{N-OH}$  orbital. (The local NO<sub>2</sub> character of the 3a"  $\pi_{nb,0}$ , 4a"  $\pi^{*}{}_{NO_{2}}$ , and the 9a'  $n_{20}$  orbitals was discussed originally by Harris<sup>23</sup> and several of the orbitals are depicted in ref. 21.) This valence bond configuration for  $\Psi_{P}$  results from the asymptotic product configuration where the NO<sub>2</sub>(1<sup>2</sup>B<sub>2</sub>) (4b<sub>2</sub>  $\rightarrow$  6a<sub>1</sub>) product has two electrons in the 6a<sub>1</sub> orbital involved in forming the  $\sigma_{N-OH}$  bond with OH, which has one electron in the a' orbital involved in forming this bond.

Let us now analyze the configuration interaction matrix elements that couple the excited reactant configuration,  $\{\cdots (2a'')^2(8a')^2(9a')^2(3a'')^1(4a'')^1(10a')^0\} \approx \{\cdots (np_{OH}a'')^2(\sigma_{N-OH})^2(n_{20}a')^2(\pi_{nb,0})^1(\pi^*_{NO_2})^1(\sigma^*_{N-OH})^0\}$ , to the  ${}^{1}n_{20}\sigma^*_{N-OH}$  configuration  $\{\cdots (2a'')^2(8a')^2(9a')^1(3a'')^2(4a'')^0(10a')^1\}$  corresponding to the adiabatic asymptotic products  $NO_2$  ( $1^2B_2$ ),  $\{\cdots (4b_2)^1(1a_2)^2(6a_1)^2(2b_1)^0\} + OH$  ( $\tilde{X}^2\Pi$ , A'),  $\{\cdots (np_{OH}a'')^2(np_{OH}a')^1\}$ . Because of the symmetries of the orbitals, no one-electron matrix elements can couple the reactant and product electronic configurations:  $\langle \pi_{nb, O} | H | n_{2O} \rangle = \langle a'' | H | a' \rangle = 0$  and  $\langle \pi^*_{NO_2} | H | \sigma^*_{N-OH} \rangle = \langle a'' | H | a' \rangle = 0$ . As we have seen for bromopropionyl chloride, the one-electron resonance/exchange integrals contributing to coupling between the reactant and product electronic configurations are zero due to symmetry, leaving only two-electron integrals to couple the reactant and



Fig. 5 Molecular orbital correlation diagram showing the OH and NO<sub>2</sub> orbitals correlating to nitric acid molecular orbitals. Labels for the nitric acid orbitals are given in terms of their overall character, their planar symmetry and their local  $C_{2v}$  symmetry, with numberings from ref. 23. The symmetry and character of the NO<sub>2</sub> orbitals is also noted. Orbital occupations for the ground state of nitric acid and the ground states of products are shown, and symmetries of the orbitals are denoted with solid lines (a') or dashed lines (a'').

product electronic configurations at the avoided crossing:

$$V_{12} = 2 \langle \pi_{\rm nb, 0}(1) n_{20}(2) \left| \frac{e^2}{r_{12}} \right| \pi^*_{\rm NO_2}(1) \sigma^*_{\rm N-OH}(2) \rangle - \langle \pi_{\rm nb, 0}(1) \pi^*_{\rm NO_2}(2) \left| \frac{e^2}{r_{12}} \right| n_{20}(1) \sigma^*_{\rm N-OH}(2) \rangle$$
(2)

The two matrix elements are illustrated schematically in Fig. 6. The Förster term involves coupling between the transitions  $\pi_{nb,0} \pi^*_{NO_2}$  ( $3a'' \rightarrow 4a''$ ) and  $n_{20} \sigma^*_{N-OH}$  ( $9a' \rightarrow 10a'$ ). These excitations both involve a transition dipole moment of  $B_2$  symmetry, oriented parallel to the terminal O atoms in nitric acid. One would expect excellent coupling between these two transitions due to the similar orientation of their transition dipole moments. The second matrix element, the Dexter term, requires orbital overlap density between the  $\pi_{nb,0}(3a'')$  and  $n_{20}(9a')$  orbitals, and between the  $\pi^*_{NO_2}(4a'')$  and  $\sigma^*_{N-OH}(10a')$  molecular orbitals. These overlap densities are expected to be considerably larger than the corresponding ones for C—Br fission in bromopropionyl chloride because all four orbitals are localized on the NO<sub>2</sub> group. (Note: although the difference in symmetry results in all one-electron integrals being zero, the two-electron exchange integral here is not zero.) Thus, although the two-electron configuration interaction is modest compared to typical one-electron resonance integrals, it is large enough, because of the localization of the orbitals involved on the NO<sub>2</sub> moiety, to make us expect that



Fig. 6 Schematic diagram showing the orbitals contributing to Förster and Dexter matrix elements in  $V_{12}$ , responsible for coupling the electronic configurations involved in the observed adiabatic dissociation of nitric acid to OH ( $\tilde{X}^2\Pi$ , A') + NO<sub>2</sub> (1<sup>2</sup>B<sub>2</sub>) following  $\pi_{nb}\pi^*$  excitation. These are labelled both by their character in nitric acid and by their symmetry with respect to the molecular plane. The relative importance of these matrix elements is discussed in the text.

some molecules might be able to traverse the avoided crossing adiabatically. Indeed, our experiments showed that about one third of the N-OH bond fission products were the adiabatic  $NO_2(1^2B_2) + OH$  products. However, because the configuration interaction is still modest, some nonadiabaticity (molecules retaining  $\pi\pi^*$  character through the avoided crossing) is expected; this likely helps the second  $NO_2 + OH$  channel to be competitive.

We now turn our attention to understanding the experimental result that the second channel is neither of the energetically proximate A' asymptotes, neither  $OH + NO_2$  ( $1^2B_1$ ) nor  $OH + NO_2$  ( $1^2A_2$ ). The meager intuition developed for nonadiabatic channels in the literature to date suggests that if the diabatic product-channel [here  $OH + NO_2$  ( $2^2B_2$ ); the  $2^2B_2$  state of  $NO_2$  has  $\pi_{nb, O} \pi^*_{NO2}$  character<sup>24</sup>] is not energetically allowed, as is the case for nitric acid at 193 nm, we should consider the possibility of a nonadiabatic hop from the initially excited  $2^1A'$  potential energy surface to another energetically proximate  ${}^1A'$  potential energy surface, perhaps the  $3^1A'$  or  $4^1A'$  potential energy surface shown in Fig. 4. However, the usual adiabatic correlation diagram in Fig. 4 shows the  $3^1A'$  and  $4^1A'$  surfaces correlating to  $OH + NO_2$  ( $1^2A_2$ ) and  $OH + NO_2$  ( $1^2B_1$ ), respectively, but neither of these product channels is observed experimentally. We will now analyze the electronic changes required to access these two product channels to show why, although they are energetically allowed, they are electronically inaccessible. The answer to why these products are not formed lies in considering the drastic electronic changes required to produce these NO<sub>2</sub> electronic states.

We consider first the electronic changes necessary to produce NO<sub>2</sub>  $(1^2B_1) + OH$  $(\tilde{X}^2\Pi, A'')$  following a nonadiabatic hop from the initially excited  $2^1A'$  surface to the product region of the  $4^1A'$  surface. The electronic configuration must change from predominantly  $\{\cdots(2a'')^2(8a')^2(9a')^2(3a'')^1(4a'')^1(10a')^0\} \approx \{\cdots(np_{OH}a'')^2(\sigma_{N-OH})^2(n_{2O}a')^2(\pi_{nb,O})^1(\pi^*_{NO2})^1(\sigma^*_{N-OH})^0\}$  in the reactants to the dominant product configuration,  $\{\cdots(2a'')^1(8a')^1(9a')^2(3a'')^1(10a')^1\}$ , corresponding to the adiabatic asymptotic products NO<sub>2</sub>  $(1^2B_1)$ ,  $\{\cdots(4b_2)^2(1a_2)^2(6a_1)^0(2b_1)^1\} + OH$   $(\tilde{X}^2\Pi, A'')$ ,  $\{\cdots(np_{OH}a')^2(np_{OH}a'')^1\}$ . The two-electron configuration interaction matrix elements responsible for coupling these configurations are:

$$V_{12} = 2 \langle \sigma_{\rm N-OH}(1) n p_{\rm OH} a''(2) \left| \frac{e^2}{r_{12}} \right| \pi_{\rm nb, O}(1) \sigma^*_{\rm N-OH}(2) \rangle - \langle \pi_{\rm nb, O}(1) \sigma_{\rm N-OH}(2) \left| \frac{e^2}{r_{12}} \right| n p_{\rm OH} a''(1) \sigma^*_{\rm N-OH}(2) \rangle$$
(3)

The first matrix element, the Förster term (depicted in the top frame of Fig. 7), involves coupling transition dipoles of  $a_2$  [NO<sub>2</sub> (de)excitation] and  $b_1$  (OH excitation) local  $C_{2v}$  symmetry, so contributions from this term are very small. The Dexter term, depicted in the bottom frame of Fig. 7, is also poor. The electron density in the  $\pi_{nb, O}$  orbital is localized on the two terminal O atoms of the NO<sub>2</sub> group, while the np<sub>OH</sub>a" orbital is localized on the O atom of the OH, so the orbital overlap density  $\pi_{nb, O}(1)np_{OH}a"(1)$  product in the integrand is nearly zero at all  $r_1$ . The Dexter matrix element is thus approximately zero. The minimal contributions to the off-diagonal coupling elements from both matrix elements lead us to expect that the electronic wavefunction cannot adjust to produce these electronic states of products.

For the electronic wavefunction to undergo a nonadiabatic hop to the product configuration on the 3<sup>1</sup>A' surface, the dominant electronic configuration on the NO<sub>2</sub> moiety must change from  $\pi_{nb}\pi^*$  in the Franck–Condon region to  $\pi_{nb}\sigma^*_{N-OH}$ , while the electronic configuration on OH must change from  $np_{OH}a''$  to  $\sigma^*_{N-OH}$  in order for the parent wavefunction to maintain overall A' symmetry. This change in electronic configuration corresponds to changing from  $\Psi_R = \{\cdots (2a'')^2(8a')^2(9a')^2(3a'')^1(4a'')^1(10a')^0\} \approx$  $\{\cdots (np_{OH}a'')^2(\sigma_{N-OH})^2(n_{20}a')^2(\pi_{nb, 0})^1(\pi^*_{NO2})^1(\sigma^*_{N-OH})^0\}$  to  $\Psi_P = \{\cdots (2a'')^1(8a')^2(9a')^2(3a'')^1(4a'')^0(10a')^2\}$ , corresponding to the adiabatic asymptotic products  $NO_2(1^2A_2)$ ,  $\{\cdots (4b_2)^2(1a_2)^1(6a_1)^2(2b_1)^0\} + OH(\tilde{X}^2\Pi, A'')$ ,  $\{\cdots (np_{OH}a'')^2(np_{OH}a'')^1\}$ . Here, the Förster term involves coupling of transition dipoles both of b\_1 symmetry  $(\pi^*_{NO2}\sigma^*_{N-OH})$ 



Fig. 7 Schematic diagram showing the orbitals contributing to Förster and Dexter matrix elements in  $V_{12}$ , responsible for coupling the initially excited  $\pi_{nb}\pi^*$  electronic configuration to the unobserved dissociation channel leading to OH ( $\tilde{X}^2\Pi$ , A") + NO<sub>2</sub> (1<sup>2</sup>B<sub>1</sub>) formation. The orbitals are labelled both by their character in nitric acid and by their symmetry with respect to the molecular plane. This coupling is exceedingly weak, as discussed in the text.

and  $np_{OH} a'' \sigma^*_{N-OH}$ , which could be significant. However, in systems such as this where the transition dipoles and chromophore separation are relatively small, the electronic energy transfer has been found to be governed by short-range exchange interactions.<sup>11b,25</sup> Thus, we can look to the Dexter, or exchange term, to see the strength of the configuration coupling. This requires orbital overlap densities between  $\sigma^*_{N-OH}$  and  $np_{OH}a''$ , and between  $\pi^*_{NO_2}$  and  $\sigma^*_{N-OH}$ . Fig. 8 shows both the Förster and Dexter matrix elements, described in terms of their local NO<sub>2</sub> and OH molecular orbitals to make the valence bond treatment clearer. The Dexter term requires orbital overlap between the  $2b_1(\pi^*)$  orbital on NO<sub>2</sub> and the  $np_{OH}a'$  orbital on OH, and between the  $6a_1$ orbital on NO<sub>2</sub> and the  $np_{OH}a''$  orbital on OH. While these terms are expected to both be significant because of the spatial proximity of the NO<sub>2</sub> and OH moieties in nitric acid, at larger separations where the avoided crossing of these configurations likely occurs, the overlap is diminished and this channel becomes electronically inaccessible.

The approach used here to determine whether or not energetically close product asymptotes are electronically accessible has led us to conclude that the configuration interaction matrix elements responsible for coupling configurations representing changes on two spatially separated functional moieties are very small; thus such product channels are electronically inaccessible. For dissociation from the low-lying excited states of nitric acid leading to product channels accessible energetically at 193 nm (all of which require configuration changes on the NO<sub>2</sub> group), the electronically inaccessible product asymptotes are ones where the number of electrons in what will become the in-plane nonbonding OH  $\pi$  orbital must change from one to two as the reactant configuration evolves to the product configuration. Thus, for the low-lying excited states of nitric acid, we restrict the accessible product channels to include only asymptotes where the OH product is in the OH( $\tilde{X} \, {}^2\Pi$ , A') state. The resulting 'restricted adiabatic' correlation diagram, shown in Fig. 9, gives a better prediction of the experimentally observed OH + NO<sub>2</sub> product channels from nitric acid at 193 nm than the traditional adiabatic



Fig. 8 Schematic diagram showing the orbitals contributing to Förster and Dexter matrix elements in  $V_{12}$ , responsible for coupling the initially excited  $\pi_{nb}\pi^*$  electronic configuration to the unobserved dissociation channel leading to OH ( $\tilde{X} \,^2\Pi$ , A'') + NO<sub>2</sub> (1<sup>2</sup>A<sub>2</sub>) formation. Here, we label the orbitals by their asymptotic NO<sub>2</sub> and OH product molecular orbital designations, in order to clarify which orbitals are occupied in the product fragments. This coupling to the initially excited configuration is weak, as discussed in the text.

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Fig. 9 'Restricted' correlation diagram for the dissociation of nitric acid to  $OH + NO_2$  at bent  $NO_2$  geometries. The energies and labels are as in Fig. 4. Solid lines indicate states of A' symmetry and dashed lines indicate states of A'' symmetry with respect to the nitric acid molecular plane. Here, the lightly dotted lines indicate formation of  $OH(\tilde{X}^2P, A'')$ , arising from occupation of the  $\sigma^*_{C-N}$  orbital in nitric acid. These states lie much higher in energy than those depicted here, and we neglect them due to the weak off-diagonal coupling for formation of this electronic configuration from the initial excitation. Adapted with permission from Fig. 13 of ref. 12.

correlation diagram which correlates to both possible symmetries of OH products. Correlation to NO<sub>2</sub> + OH( $\tilde{X}^2\Pi$ , A") only occurs in the restricted adiabatic correlation diagram from higher lying valence bond states of nitric acid that have an electron in the  $\sigma^*_{N-OH}$  orbital (shown by dotted lines in Fig. 9). This 'restricted adiabatic' correlation diagram still allows for the adiabatic formation of NO<sub>2</sub> (1<sup>2</sup>B<sub>2</sub>) + OH( $\tilde{X}^2\Pi$ ) following  $\pi_{nb, 0}\pi^*_{NO_2}$  excitation (as this requires configuration changes localized on one functional group), in agreement with one of our experimentally observed channels, but it disallows dissociation within overall A' symmetry to the product channels which did not occur experimentally, OH + NO<sub>2</sub> (1<sup>2</sup>B<sub>1</sub>) and OH + NO<sub>2</sub> (1<sup>2</sup>A<sub>2</sub>). Further support for these ideas is afforded by the photodissociation of nitromethane at 193 nm in the analogous  $\pi_{nb, 0}\pi^*_{NO_2}$  absorption; that also results in NO<sub>2</sub>(1<sup>2</sup>B<sub>2</sub>) but not NO<sub>2</sub> (1<sup>2</sup>B<sub>1</sub>) or NO<sub>2</sub> (1<sup>2</sup>A<sub>2</sub>) formation. Since the full correlation diagram of nitromethane is analogous to the restricted adiabatic correlation diagram proposed here for the low-lying states of nitric acid, this provides further support for restricting the products to asymptotes where the OH radical orbital lies in the plane (as in the radical methyl product of nitromethane).

We now have a system in which one can identify what product channels are electronically accessible to a molecule after initial electronic excitation. By examining the off-diagonal matrix elements responsible for coupling the diabatic electronic configurations, we can learn a lot about what changes in the electronic wavefunction are necessary to traverse various adiabatic and nonadiabatic pathways. Small couplings result in exclusion of channels from consideration as possible reaction pathways, which limits the electronic states under consideration as possible products. When initial electronic excitation is localized on one portion of a molecule, and subsequent product formation requires changes in both the initially excited moiety and in one excluded from this initial excitation, consideration of the off-diagonal matrix coupling elements shows that dissociation into these product channels is extremely improbable. A 'restricted adiabatic' correlation diagram can then be used for additional insight into possible (and more probable) reaction channels.

# 3 Testing the model: the HCO + $N(CH_3)_2$ product channel from the 193 nm photodissociation of N,N-dimethylformamide

Thus far we have shown that, for both adiabatic and nonadiabatic product channels, one must analyze not only whether the potential product channel is energetically allowed, but also whether it is electronically accessible from the excited reactant electronic configuration. If the reactant and product electronic configurations can be coupled by the typically substantial one-electron configuration interaction matrix elements, then that product channel is electronically accessible. If these matrix elements are zero (perhaps, due to symmetry), then one expects nonadiabatic dynamics to effectively compete with the adiabatic channel, but products which involve configuration changes where the orbitals are localized on one functional moiety are still electronically accessible. The channels, adiabatic or nonadiabatic, which are electronically inaccessible are ones where both the one-electron configuration interaction matrix elements are zero and the two-electron configuration interaction integrals require configuration changes on two spatially separated functional groups. We now pursue an experiment on the photodissociation of N,N-dimethylformamide to test this proposed hierarchy of which product channels are electronically accessible. A full description of the experimental results will be published elsewhere;<sup>26</sup> here, we wish to focus on the HCO +  $N(CH_3)_2$ bond fission channel.

#### 3.1 Experimental method

The photodissociation experiments consist of two parts. We first photodissociate the N,N-dimethylformamide molecules using unpolarized 193 nm light. We detect ionized dissociation products as a function of their m/z ratio and times-of-flight using a crossed laser-molecular beam apparatus.<sup>27</sup> This allows us to determine the recoil translational energy distributions of the fragments formed in the dissociation process. We then polarize the laser light and detect signal for a selected dissociation channel in order to learn about the angular distribution of the photofragmentation process.

We used N,N-dimethylformamide as obtained from Fisher Scientific (99.9% purity) and degassed it prior to flowing the beam. Helium was bubbled through it (at 56 °C) to provide an 8% seeded beam with a total stagnation pressure of 300 Torr, which was then expanded through a 0.12 mm diameter nozzle, heated to 235 °C. This high nozzle temperature was required to reduce the presence of clusters in the supersonic expansion. To measure the velocity of the parent molecular beam *in situ*, we rotated the molecular beam source to point into the detector and raised a chopper wheel into the beam. The peak beam velocity was  $1.75 \times 10^5$  cm s<sup>-1</sup> with a full width at half-maximum (FWHM) of 18.3%. Quadrupole resolution was adjusted to roughly 1.0 for all masses.

After photodissociation with a pulsed excimer laser, neutral dissociation products scatter from the crossing point of the laser and the molecular beam with velocities determined by the vector sum of the molecular beam velocity and the recoil velocity imparted during dissociation. Fragments scattered into the  $1.5^{\circ}$  acceptance angle of the detector travel 44.13 cm and are ionized by 200 eV electrons. After mass selection with a quadrupole mass filter, the ions are counted with a Daly detector and recorded with a multichannel scaler with respect to their time-of-flight (TOF) from the interaction region after the dissociating laser pulse. Forward convolution fitting of the TOF spectrum determines the distribution of energies released to relative product translation in the dissociation. Molecular beam source angles are given here with respect to the detector axis. The plane defined by the molecular beam and the detector axis is perpendicular to the direction of laser propagation.

In order to determine the extent of clusters present in the expansion, we examined the parent beam TOF signal at N,N-dimethylformamide (m/z = 73) and at this mass plus one (m/z = 74) by rotating the molecular beam source to point into the detector and raising the chopper wheel into the beam. Since the signal observed at m/z = 74cannot arise from monomers in our beam, we attributed this signal to clusters and tried to eliminate it. Raising the nozzle temperature reduced the signal at m/z = 74, thus reducing the contribution of clusters to the beam. We identified all remaining signal due to the photodissociation of clusters by taking photofragment TOF data (at angles tilted for the molecular beam) at the spectral monomer of the clusters, m/z = 73, a mass that cannot arise from dissociation of the true monomer.

A Lumonics PM-848 excimer laser filled with ArF produced the 193 nm light used to photodissociate the N,N-dimethylformamide molecules. The laser beam was focussed to give an attenuated laser energy of 6 mJ pulse<sup>-1</sup> and a 6 mm<sup>2</sup> spot size in the crossing region with the molecular beam. In order to generate polarized light, we dispersed the unpolarized laser light into two linearly polarized components with a single crystal quartz Pellin–Broca prism. We used the horizontal component and rotated the polarization into the desired direction with a half-wave retarder. For these polarized experiments, the output pulse energy was power-locked to 1.6 mJ pulse<sup>-1</sup> in the interaction region. In order to avoid any systematic errors in determining the anisotropies of the scattered photofragments, we measured the polarization dependent signal by taking many repeated short scans of 50 000 laser shots each, alternating between each laser polarization direction, for a total of 200 000 laser shots. Because of these averaging techniques, no additional normalization to laser power or detector efficiency was necessary. Lab polarization angles are measured in the opposite direction as source rotation angles for the data shown here; both are measured with respect to the detector axis.

## 3.2 Identification of primary product channels: primary N–CO and N–CH<sub>3</sub> bond fission in N,N-dimethylformamide

The data recorded in this experiment lead us to assign two competing channels for the photodissociation of N,N-dimethylformamide:<sup>26,28</sup>

 $\text{HCON}(\text{CH}_3)_2 + 193 \text{ nm} \rightarrow \text{HCO} + \text{N}(\text{CH}_3)_2 \qquad \Delta H^\circ = 94.4 \pm 1.5 \text{ kcal mol}^{-1} \quad \text{(I)}$ 

$$\text{HCONCH}_3 + \text{CH}_3 \quad \Delta H^\circ \approx 80 \text{ kcal mol}^{-1} \tag{II}$$

In this paper, we present our results on reaction (I), hereafter referred to as breaking the 'N-CO bond'. The results on the second product channel are in preparation for publication.<sup>26</sup> To assign the product channels, we fit the data collected at various m/z ratios to translational energy distributions. Because of extensive fragmentation in the electronbombardment ionizer, many different daughter ions arise from the same parent photofragment. By momentum matching signals from heavy and light partner fragments (and their possible daughter ions) in the forward convolution fitting of our data, one can unambiguously identify the signal at each possible daughter ion with its corresponding parent photofragment for each of the product channels. Fig. 10 shows two TOF spectra, the top one taken at m/z = 42 ( $C_2H_4N^+$ , CON<sup>+</sup>) and the bottom one taken at m/z = 29 (HCO<sup>+</sup>, CH<sub>3</sub>N<sup>+</sup>). We fit the fast signal at m/z = 42 to a photofragment translational energy distribution [P( $E_T$ )] corresponding to formation of HCO + N(CH<sub>3</sub>)<sub>2</sub>, as shown in Fig. 11. We assigned this signal to N—CO bond fission because of the presence of the momentum-matched formyl fragment in the signal observed at m/z = 29. We were also able use the same P( $E_T$ ) to fit signals arising from other daughter fragments of m/z = 44 (CH<sub>3</sub>NCH<sub>3</sub><sup>+</sup>) [at m/z = 29 (NCH<sub>3</sub><sup>+</sup>), and at m/z = 43 (CH<sub>3</sub>NCH<sub>2</sub><sup>+</sup>) and 15 (CH<sub>3</sub><sup>+</sup>), not shown].

The energy required for N-CO bond fission (94 kcal mol<sup>-1</sup>) plus the translational energy distributed between the photoproducts ( $E_T < 31 \text{ kcal mol}^{-1}$ ) is less than that available from the 193 nm photons (148 kcal mol<sup>-1</sup>). This excess energy, taken with the fact that the translational energy distribution peaks away from zero, can indicate formation of electronically excited products.<sup>12</sup> We are interested to know whether this dis-



**Fig. 10** Time-of-flight data, recorded following N,N-dimethylformamide photodissociation at 193 nm, with a 10° source angle with respect to the detector axis. The top figure shows signal recorded at m/z = 42 (arising from CON<sup>+</sup> and C<sub>2</sub>H<sub>4</sub>N<sup>+</sup> ions), and the bottom figure shows signal recorded at m/z = 29 (arising from HCO<sup>+</sup> and CH<sub>3</sub>N<sup>+</sup> ions). Open circles show experimental data points; dashed lines show the fits arrived at with the product kinetic energy distributions for N-CO bond fission (Fig. 11) and N-CH<sub>3</sub> bond fission (ref. 26). The total fit is shown by the solid black line.



**Fig. 11** Centre-of-mass recoil kinetic energy distribution for the observed HCO +  $N(CH_3)_2$  reaction products, determined from forward convolution fitting of the signal from N-CO bond fission in the TOF spectrum in Fig. 10. The arrow denotes the maximum available energy for translation if  $N(CH_3)_2$  were formed in its first excited state ( $\tilde{A}^2A_1$ ), assuming it to have similar electronic energetics to the unsubstituted NH<sub>2</sub> radical. (NH<sub>2</sub> energy from ref. 30.)

sociation forms electronically excited HCO or N(CH<sub>3</sub>)<sub>2</sub>, since a preference for one over the other can address the issue of the electronically accessible product channels in this reaction. Experiments and calculations have shown that HCO formed with internal energy above 16 kcal  $mol^{-1}$  dissociates on a nanosecond (or shorter) time scale to  $H + CO^{29}$  The signal we observe at m/z = 29 (surviving after a flight time longer than 100 µs) must therefore arise from formyl radicals formed with a low amount of internal energy. Since our signal at m/z = 29 can be fully fit with the P( $E_T$ ) assigned to the daughter fragments of the momentum-matched partner  $[N(CH_3)_2]$ , it accounts for all of the HCO initially formed from the dissociation, *i.e.*, there is no evidence in our data for formation of electronically excited (or highly internally excited ground-state) HCO which would undergo subsequent predissociation. Thus, we assign the observed N-CO bond fission channel to HCO( $\tilde{X}^2 A'$ ) + N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{A}^2 A_1$ ). For that product channel, most of the excess energy goes into electronic excitation of N(CH<sub>3</sub>)<sub>2</sub>, explaining why the observed kinetic energy distribution stops short of the energetic limit for ground state formation of products by over 23 kcal mol<sup>-1</sup>. Unfortunately, the energy of electronically excited dimethylamidogen, N(CH<sub>3</sub>)<sub>2</sub>, is not known, though we can estimate its energetics by comparing it with the unsubstituted radical NH<sub>2</sub>. NH<sub>2</sub> has a low-lying electronically excited state  $(\tilde{A}^2A_1)$  that lies 1.38 eV above ground state  $NH_2(\tilde{X}^2B_1)$ .<sup>30</sup> If the minimum of the  $\tilde{A}$  state of the N(CH<sub>3</sub>)<sub>2</sub> radical were the same as that for NH<sub>2</sub> ( $\tilde{A}^2A_1$ ), the maximum energy available for relative translation of that product would be  $E_{max} \approx$ 22 kcal mol<sup>-1</sup>. This limit is shown by an arrow on Fig. 11. It is possible that the  $\tilde{A}$  state of  $N(CH_3)_2$  is red-shifted from that of  $NH_2$ , allowing the recoil energy distribution to extend to a somewhat higher energy, as supported by our fit.

#### 3.3 Angular distribution of the HCO + $N(CH_3)_2$ dissociation products

In order to fit the photofragment angular distributions recorded at the six laser polarization angles, we vary the anisotropy parameter,  $\beta$ , in the classical electric dipole expression<sup>31</sup> for the signal intensity,  $\omega$ , in the center-of-mass reference frame as a function of the laser polarization angle

$$\omega(\theta_{\rm CM}) = (1/4\pi)[1 + \beta P_2(\cos \theta_{\rm CM})] \tag{4}$$

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until, after converting the prediction to the lab frame, the shape of the distribution matches that obtained from integration of our signal intensity. Because  $\theta_{CM}$  is the angle between the recoil direction of the detected photofragment in the center-of-mass reference frame and the electric vector of the light, fitting the data involves converting between the center-of-mass and lab frames using the measured molecular beam velocity and the P( $E_T$ ) derived from the unpolarized data. Fig. 12 shows a plot of the signal intensity at m/z = 42, integrated from 166 to 218 µs, assigned to N—CO bond fission, vs.  $\theta_{LAB}$ , the angle between the laser electric vector and the detector axis. Error bars, determined by a Poisson counting error, are smaller than the dots in Fig. 12 used to represent the data points. Theoretical fits for three different values of  $\beta$  are shown, and it can be seen that  $\beta = 1.4$  for the N-CO bond fission channel gives the best agreement with the experimental intensity.

In the limit of prompt axial recoil, the anisotropy parameter  $\beta$  can be related to the angle  $\alpha$  between the transition dipole moment  $\mu$  and the bond that is breaking through the relation

$$\beta = 2P_2(\cos \alpha). \tag{5}$$

The value of  $\beta$  can range from 2 for a parallel transition (giving a  $\cos^2\theta$  distribution of products) to -1 for a perpendicular transition (giving a  $\sin^2\theta$  angular distribution). Using the transition dipole moment obtained from CASSI *ab initio* calculations,<sup>32</sup> we calculate a predicted value of  $\beta = 1.74$ . The close agreement between this and the observed  $\beta$  shows that the dissociation to HCO + N(CH<sub>3</sub>)<sub>2</sub> is occurring on a rapid timescale that is fast with respect to molecular rotation.

#### 3.4 Discussion

To treat electron configurations in *N*,*N*-dimethylformamide, we can follow the treatment of Nagakura<sup>33,34</sup> and write the electronic configurations contributing to both the ground state and first  $\pi\pi^*$  excited state in terms of the occupation of three local  $\pi$ orbitals,  $\pi$  and  $\pi^*$  localized on the C=O moiety and  $\pi_{nb}$  localized on nitrogen. Fig. 13



Fig. 12 Integrated intensity of the early signal at m/z = 42, corresponding to the nitrogen—carbonyl fission channel, versus the laser polarization angle. Dots show the experimental points (error bars fall within the size of these points; see text). The curves are based on calculated intensities for various values of  $\beta$ , smoothed with a cubic spline fit.  $\beta = 1.4 \pm 0.1$  was assigned based on agreement with experimental data points.



Fig. 13 Schematic illustrating the three electronic configurations contributing to the  $\pi_{nb}\pi^*$  state in *N*,*N*-dimethylformamide

shows the contributing configurations, labelled the zeroth-order ground configuration (GC)  $[(\pi)^2(\pi_{nb})^2(\pi^*)^0]$ , the charge transfer (CT) configuration  $[(\pi)^2(\pi_{nb})^1(\pi^*)^1]$  and the locally excited (LE) configuration  $[(\pi)^1(\pi_{nb})^2(\pi^*)^1]$ . Nagakura forms the ground and excited states of HCONH<sub>2</sub> by taking linear combinations of these three configurations. His simple model gives

$$\Psi_0 = 0.89 \Psi_{GC} + 0.46 \Psi_{CT} - 0.07 \Psi_{LE}$$
$$\Psi_1 = 0.44 \Psi_{GC} - 0.78 \Psi_{CT} + 0.46 \Psi_{LE}$$

in the Franck–Condon region for formamide.<sup>33</sup> In N,N-dimethylformamide, the ground state and the 3<sup>1</sup>A' state reached upon  $\pi_{nb}\pi^*$  excitation (analogous to  $\Psi_1$  above) each have considerable contributions from both the zeroth-order ground state configuration and the charge-transfer configuration. Recent CASSCF calculations have shown that the charge-transfer character of this nominally  $\pi\pi^*$  state (3<sup>1</sup>A') in N,N-dimethylformamide amounts to moving only 0.3–0.4 e<sup>-</sup> from nitrogen to the carbon relative to the 1<sup>1</sup>A' ground state.<sup>32</sup> (The importance of the charge-transfer configuration in amides has been well studied. See also ref. 35–37 for experimental and theoretical studies documenting its contribution to this  $\pi\pi^*$  state.)

It is obvious from this treatment that we cannot treat the  $3^{1}A'$  state accessed at 193 nm as a pure state in terms of these localized orbitals. Instead, there is already in the Franck–Condon region strong one-electron coupling between these configurations, resulting in SCF wavefunctions with contributions combining these zeroth-order natural orbital configurations.<sup>32</sup> It is important, however, to identify the approximate *diabatic* correlations from each of the zeroth-order configurations involved in the  $\tilde{X}^{1}A'$  and  $3^{1}A'$  states in the Franck–Condon region, to the electronic states of HCO + N(CH<sub>3</sub>)<sub>2</sub> products. These are:

$$\begin{split} \Psi_{GC} &= \{ \cdots (\sigma_{C-N})^2 (\pi)^2 (\pi_{nb})^2 (\pi^*)^0 (\sigma^*_{C-N})^0 \} \\ &\approx HCO(\tilde{X}\,^2A') \{ \cdots (1a'')^2 (7a')^1 (2a'')^0 \} + N(CH_3)_2 (\tilde{A}^2A_1) \{ \cdots (3a_1)^1 (1b_1)^2 \} \\ \Psi_{CT} &= \{ \cdots (\sigma_{C-N})^2 (\pi)^2 (\pi_{nb})^1 (\pi^*)^1 (\sigma^*_{C-N})^0 \} \\ &\approx HCO^{*-} \{ \cdots (1a'')^2 (7a')^1 (2a'')^1 \} + N(CH_3)_2^+ \{ \cdots (3a_1)^1 (1b_1)^1 \} \\ \Psi_{LE} &= \{ \cdots (\sigma_{C-N})^2 (\pi)^1 (\pi_{nb})^2 (\pi^*)^1 (\sigma^*_{C-N})^0 \} \\ &\approx HCO^* (^2A') \{ \cdots (1a'')^1 (7a')^1 (2a'')^1 \} + N(CH_3)_2 (\tilde{A}^2A_1) \{ \cdots (3a_1)^1 (1b_1)^2 \} \end{split}$$

[The HCO molecular orbital labels follow Tanaka and Davidson;<sup>38</sup> for  $N(CH_3)_2$  we have used molecular orbital labels of  $NH_2$ .] An approximate energy level diagram for the dissociation of *N*,*N*-dimethylformamide to HCO +  $N(CH_3)_2$  is shown in Fig. 14.



Fig. 14 Energy level diagram showing the relative energies of the electronic states of N,Ndimethylformamide and possible HCO + N(CH<sub>3</sub>)<sub>2</sub> products. The energetic ordering of the two closely spaced energy levels for formation of HCO + N(CH<sub>3</sub>)<sub>2</sub>, where one of these radicals is in its first excited state, is uncertain. In estimating the  $\tilde{A}$  state energy of N(CH<sub>3</sub>)<sub>2</sub>, we have used the energy of the  $\tilde{A}$  state of NH<sub>2</sub>, given as 11 125.78 cm<sup>-1</sup> in ref. 30. HCO electronic energies are from ref. 38; vertical HCON(CH<sub>3</sub>)<sub>2</sub> electronic energies are from ref. 32. Because of the close energetic spacing of the excited N,N-dimethylformamide states, we show an expanded view of those in the vicinity of the 3<sup>1</sup>A' state accessed in our experiments. Solid lines indicate states of A' symmetry and dashed lines indicate states of A'' symmetry with respect to the heavy atom molecular plane.

Neither the diabatic asymptote of  $\Psi_{CT}$  (the ion pair) nor the diabatic asymptote of  $\Psi_{LE}$  (involving a high-lying HCO excited state) is energetically accessible. According to our energy level diagram (Fig. 14), there are three product states which are energetically accessible and another which is just barely out of range, using the NH<sub>2</sub> electronic energies. Experimentally, only formation of HCO( $\tilde{X}^2A'$ ) + N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{A}^2A_1$ ) is observed; we now analyze why the other channels do not compete.

The reactant  $3^{1}A'$  state in the Franck–Condon region is comprised of an electronic configuration,  $\Psi_{GC}$ , that is already the configuration of the experimentally observed  $HCO(\tilde{X}^{2}A') + N(CH_{3})_{2}(\tilde{A}^{2}A_{1})$  product channel, and an electronic configuration,  $\Psi_{CT}$ , that is strongly coupled by one-electron matrix elements to that product electronic configuration. Thus, the electronic changes required to access the observed product channel are strongly allowed; this product channel is 'electronically accessible' in the model developed from the prior experiments. Because this is the observed channel, and because its formation ranks high on our hierarchy of electronic coupling strengths, it is unlikely that the configurations of any of the other energetically accessible product channels are strongly coupled to the initially excited configuration. We shall examine these other channels now to see if this is the case.

The energetically proximate A' channel, leading to formation of HCO( $\tilde{A}^2 A''$ ) + N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{X}^2 B_1$ ), was not observed experimentally. To understand why this is so, we can first examine the electronic changes necessary for the initially excited wavefunction to access these products. None of the contributing configurations to the 3<sup>1</sup>A' state,  $\Psi_{GC}$ ,  $\Psi_{CT}$ , nor  $\Psi_{LE}$ , has the correct configuration to correlate diabatically with formation of HCO( $\tilde{A}^2 A''$ ) + N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{X}^2 B_1$ ). The charge-transfer state can couple to this neutral product channel through a one-electron transition promoting an electron from the  $\sigma_{C-N}$  orbital to the  $\sigma^*_{C-N}$  orbital [in the local picture, from HCO back to N(CH<sub>3</sub>)<sub>2</sub>, 7a'  $\rightarrow$  3a<sub>1</sub>], resulting in what we term the double charge transfer (DCT) configuration,

$$\begin{split} \Psi_{\text{DCT}} &= \{ \cdots (\sigma_{\text{C}-\text{N}})^1 (\pi)^2 (\pi_{\text{nb}})^1 (\pi^*)^1 (\sigma^*_{\text{C}-\text{N}})^1 \} \\ &\approx \text{HCO}(\tilde{A}^2 A'') \{ \cdots (1a'')^2 (7a')^0 (2a'')^1 \} + \text{N}(\text{CH}_3)_2 (\tilde{X}\,^2\text{B}_1) \{ \cdots (3a_1)^2 (1b_1)^1 \} \end{split}$$

This state can also be accessed from the ground configuration *via* a two-electron transition, as depicted in Fig. 15. Although this avoided configuration crossing between  $\Psi_{DCT}$  and  $\Psi_{GC}$  is likely to be energetically accessible, the two-electron matrix elements coupling  $\Psi_{GC}$  and  $\Psi_{DCT}$  are expected to be small, so that the avoided crossing is traversed diabatically, resulting in HCO( $\tilde{X}^2A'$ ) + N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{A}^2A_1$ ), the experimentally observed product channel.

Formation of either  $HCO(\tilde{X}^2A') + N(CH_3)_2(\tilde{X}^2B_1)$  or  $HCO(\tilde{A}^2A') + N(CH_3)_2(\tilde{A}^2A_1)$  involves overall A'' symmetry with respect to the molecular plane. Since we are initially accessing the  $3^1A'$  surface, formation of these products is neither adiabatically nor nonadiabatically allowed, if the molecule may be approximated as retaining planar geometry. This is equivalent to saying that if the molecule encounters a conical intersection between an A' configuration and an A'' configuration, it retains the A' electronic character. Because N,N-dimethylformamide is planar in its ground state geometry,  $^{32,39}$  we treat the dissociation to  $HCO + N(CH_3)_2$  in this planar limit; thus, trajectories traverse any conical intersection diabatically.

We should note that a usual adiabatic correlation diagram, generated by energetically ordering the electronic states of parent and fragments, and connecting states of like symmetry, would not predict the observed product channels. The ground and  $2^{1}A'$  states of N,N-dimethylformamide would correlate to the HCO ( $\tilde{A}^{2}A''$ ) + N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{X}^{2}B_{1}$ ) and the HCO( $\tilde{X}^{2}A'$ ) + N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{A}^{2}A_{1}$ ) product channels (the energetic ordering of which is not known due to the uncertainty in the energy of the  $\tilde{A}$  state of N(CH<sub>3</sub>)<sub>2</sub>), while the  $3^{1}A'$  state of N,N-dimethylformamide excited at 193 nm would correlate adiabatically to energetically inaccessible products at 193 nm. These correlations depend on the relative ordering, not only of the HCO ( $\tilde{A}$ ) and N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{A}$ ) states, but also of the  $2^{1}A'$  and  $3^{1}A'$ states of N,N-dimethylformamide. In the Franck–Condon region, these electronic states are almost degenerate in energy, but  $2^{1}A'$ , corresponding to a  $16a' \rightarrow 3s$  Rydberg transition, is calculated to lie slightly lower in energy, by 0.08 eV at the CAS level and by 0.02 eV at the PT2 level of theory.<sup>32</sup> The overwhelming oscillator strength of the nomin-



Fig. 15 Schematic showing the orbitals contributing to Förster and Dexter coupling in  $V_{12}$  for dissociation of the  $\Psi_{GC}$  component of HCON(CH<sub>3</sub>)<sub>2</sub> (3<sup>1</sup>A') to the experimentally unobserved channel HCO( $\tilde{A}^2A''$ ) + N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{X}^2B_1$ ), requiring double charge transfer. Here, we label the orbitals by their asymptotic N(CH<sub>3</sub>)<sub>2</sub> and HCO product molecular orbital designations in order to clarify the valence bond construction of the double charge transfer state,  $\Psi_{DCT}$ .

ally  $\pi\pi^*$  transition ensures that we are accessing the  $\pi_{nb}\pi^*$  state at 193 nm, not the Rydberg state.

### 4 Summary

The ability of an electronic wavefunction to change its character en route to dissociation depends on the configuration interactions between the electronically excited parent and the fragment species. In cases where the electronic configurations of fragments are not diabatically correlated with the initial parent configuration, the experiments described here demonstrate the importance of considering the off-diagonal configuration interaction matrix elements involved in coupling these configurations. The magnitude of this coupling can exert considerable control over the dissociation dynamics of the molecule, influencing whether an energetically allowed product channel is electronically accessible, *i.e.* whether the electronic wavefunction can change *en route* to dissociation to the electronic configuration of the product. In a qualitative hierarchy of what electronic changes are possible, we propose that products requiring two-electron configuration changes involving orbitals on two spatially-separated functional groups are virtually inaccessible.

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