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Spin-forbidden dehydrogenation of methoxy cation: a statistical view

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A non-adiabatic version of RRKM theory is applied to predicting the microcanonical rates for different mechanisms of spin-forbidden dissociation of methoxy cation and its isotopically substituted derivatives, to formyl cation and dihydrogen. The predictions are in agreement with experimental results on this system, and in particular with the occurrence of a "direct" mechanism for dissociation, rather than of an indirect one *via* hydroxymethyl cation. *Ab initio* computations were used throughout to provide the parameters needed to apply the non-adiabatic RRKM theory, and the success of this strategy is shown to be promising for other applications in polyatomic systems. Finally, the kinetic energy release distribution for loss of hydrogen from methoxy and hydroxymethyl cations are computed using *ab initio* "direct dynamics" classical trajectories at the HF/6-31G** level, their similarity is also in agreement with experiment.

1. Introduction

In a recent Communication,[1] we presented some new experimental results concerning the metastable dehydrogenation reaction of methoxy cation, CH_3O^+, as well as a new interpretation of these and previous results. Based on an analysis of the isotope effects in the reactions of various deuterated derivatives $CH_{3-x}D_xO^+$, and on a computational *ab initio* study of the $[C,H_3,O]^+$ potential energy surfaces (PESs), we suggested that the reaction most likely occurs by direct loss of H_2, rather than by indirect decomposition, *via* hydroxymethyl cation CH_2OH^+. To provide more fulsome theoretical support for this new interpretation, we wish in this article to go beyond the *ab initio* study of the relevant PESs to actually predict the rate coefficients for the various decomposition pathways, thus providing a better point of comparison with experiment.

The difficulty with this aim is that the reaction under consideration is a non-adiabatic, spin-forbidden, process. The methoxy cation reactant has two unpaired electrons, and is thus a spin triplet, whereas the products, formyl cation HCO^+ and dihydrogen H_2, both have only paired electrons, so that they lie on a spin singlet PES. As shown in the *ab initio* study,[1] the spin inversion event is crucial to the occurrence of the reaction, since whatever the mechanism, the spin flip occurs in the region of highest energy along the reaction coordinate. The dynamical treatment used must therefore correctly describe the spin change, that is, it must be a non-adiabatic method.

Since global PESs for the singlet[2] and triplet $[C,H_3,O]^+$ system are not available, and would be extremely time-consuming to construct, and because *ab initio* methods are only able to give us limited information about these PESs, the method must additionally require only local information about the PESs. A theory which perfectly respects these requirements has been developed by Lorquet *et al.*,[3] and we will apply it in the present paper to the dissociation of methoxy cation. This theory was originally formulated in a partly phenomenological way, with some of the values for the parameters being assigned in an arbitrary manner. We will use *ab initio* calculations to determine all the parameters, which leads to some minor changes to the theory, which will be described in the first section. This will also show the critical role played by the minimum energy crossing point (MECP) between the PESs involved in the reaction. To provide a test of the version of the theory we will use, and especially of its reliance on *local* properties of the PESs only, we will then present results for the spin-forbidden dissociation reaction of N_2O into N_2 and $O(^3P)$, using an MECP located on analytical PESs taken from the literature. This will allow comparison with other, more rigorous, non-adiabatic dynamical approaches. In the next section, we will then present our main results concerning the dissociation of methoxy cation, followed by a discussion of possible future applications of the method to other problems. In the last section, we use other *ab initio* calculations to address another issue raised by the experiments on methoxy cation dissociation, namely the very similar kinetic energy release distributions (KERDs) obtained for this reaction, and for the related dissociation of hydroxymethyl cation.

2. Non-adiabatic RRKM

The dynamics of a non-adiabatic reaction can be treated by quantum mechanics in much the same way as one would treat an adiabatic reaction, by solving the corresponding Schrödinger equation for nuclear motion on the multiple electronic surfaces. Whilst this can be done for some reactions involving atoms and di- or triatomics,[4] this route is however not realistically feasible for most systems, so that various semiclassical approaches have been developed and their accuracy evaluated by comparison with the correct quantum solution.[5] One of the most popular of these approaches is the so-called "classical trajectories with surface-hopping" (CTSH) method,[6] which consists in moving the nuclei along classical trajectories, whilst propagating the electronic degrees of freedom in a quantal way, meanwhile allowing the system to cross from one surface to another. Whilst heuristically satisfying, and computationally much more tractable than the full quantum solution, this approach has been shown to be seriously wrong in some cases.[4] From the point of view of the present study, however, the main disadvantage of both quantum and semiclassical methods is that they require a complete specification of, or at least a very large amount of information about, all the potential energy surfaces (PESs) involved in the system under study, as well as of their couplings. For most polyatomic systems, such accurate surfaces are hard or even impossible to obtain from first principles.

The method of Lorquet *et al.*,[3] in contrast, in its most simple version, only needs *local* information about the PESs involved: the structure of the reactant, with its energy and harmonic vibrational frequencies, and the structure and energy of the MECP between the reactant and product PESs, as well as the strength of the coupling between the surfaces at that point, the slopes of the two PESs, and the harmonic frequencies corresponding to motion within the seam of crossing around the MECP. All of these can be obtained from *ab initio* computations. The reason one requires so little data is because the method is statistical in nature, and bears a close relation to adiabatic RRKM theory and to transition state theory (TST).[7] Of course, like these approaches, the non-adiabatic RRKM approach, especially in its simplest versions, will only lead to rate coefficient predictions of a qualitative or semi-quantitative nature, but this has not prevented the adiabatic versions from being of tremendous practical and theoretical use. We note that several related non-adiabatic statistical rate theories have been described in the literature, with all relying to a lesser or greater degree on the simplification introduced by assuming statistical behaviour.[8,9] The method of Lorquet *et al.* is however the most relevant to our study.

This method essentially relies on dividing the degrees of freedom into those parallel to the seam of crossing between the relevant PESs, which roughly assume the role of a harmonic bath, and the single direction orthogonal to the seam, in which a one-dimensional treatment of the non-adiabatic dynamics is performed. This leads to the following expression, which is an adapted version of formula (5.5) in ref. 3*a*, for the microcanonical rate coefficient $k(E)$ of a non-adiabatic unimolecular reaction:

$$k(E) = \frac{2}{h\rho(E)} \int_0^E \mathrm{d}E_h \, \rho^{\mathrm{MECP}}(E - E_h) p_{\mathrm{sh}}(E_h) \tag{2.1}$$

where h is Planck's constant, $\rho(E)$ is the reactant density of rovibrational states at energy E, $\rho^{\mathrm{MECP}}(E - E_h)$ is the density of rovibrational states for the degrees of freedom within the crossing seam at the MECP, E_h is the part of the available energy which is in the coordinate orthogonal to the seam. The term $p_{\mathrm{sh}}(E_h)$ is the surface-hopping probability for a single passage over the seam of crossing of the PESs, at the speed corresponding to energy E_h. In fact, for each event in which the system approaches the seam, crossing may occur either on the "way out" or on the way back, so that this probability needs to be multiplied by two, which explains the factor of 2 in eqn. (2.1). The hopping probability can be given either by the Landau–Zeener formula:

$$p_{\mathrm{sh}}^{\mathrm{Landau-Zeener}}(E - E_{\mathrm{MECP}}) = \frac{2\pi V_{12}^2}{h\,\Delta F} \sqrt{\frac{\mu_h}{2(E - E_{\mathrm{MECP}})}} \tag{2.2}$$

Or by the expression advanced by Delos:[8a]

$$p_{\mathrm{sh}}^{\mathrm{Delos}}(E - E_{\mathrm{MECP}}) = 4\pi^2 V_{12}^2 \left(\frac{2\mu_h}{\hbar^2 F\,\Delta F}\right)^{2/3} \times Ai^2\left[(E - E_{\mathrm{MECP}})\left(\frac{2\mu_h \Delta F^2}{\hbar^2 F^4}\right)^{1/3}\right] \tag{2.3}$$

In both of these formulas, μ_h is the reduced mass along $\boldsymbol{h}$, the direction orthogonal to the seam, ΔF is the norm of the difference of the gradients on the two surfaces, $|\partial V_1/\partial q - \partial V_2/\partial q|$, F is the geometric mean of the norms of the two gradients, $\sqrt{|\partial V_1/\partial q| \times |\partial V_2/\partial q|}$, E_{MECP} is the relative energy of the MECP, and Ai is an Airy function. It should be noted that both of these formulas assume that V_{12}, the coupling matrix element between the two PESs, is constant in the vicinity of the MECP, and that the potential energy on the two surfaces varies linearly along the direction of $\boldsymbol{h}$.

In the original version of the theory,[3a] the coordinates used to discuss the reaction were the normal-mode coordinates of the reactant minimum, and it was pointed out there was no guarantee that one of these would be even roughly orthogonal to the crossing seam at the MECP. In an accompanying paper,[3b] Remacle *et al.* showed that *ab initio* calculations could be used to determine the PESs in the region of the MECP, and to select more appropriate coordinates. This was however done in a partly *ad hoc* manner, and required considerable effort to generate the PESs. In fact, the "best" coordinates for describing the system in the region of the MECP can be determined in a completely systematic way from a limited number of *ab initio* calculations, as we will now describe.[10]

First, as many groups[11] including ourselves[12] have shown, it is possible to locate the MECP between two PESs by geometry optimisation using analytical gradients derived from *ab initio* calculations on the two PESs. In our approach, which is closely related to the other methods, the MECP between the two PESs $V_1(q)$ and $V_2(q)$ is found by locating a stationary point corresponding to the effective gradient given as the sum of the following two gradient-like terms:

$$\boldsymbol{f} = (V_1 - V_2)\left[\left(\frac{\partial V_1}{\partial q}\right) - \left(\frac{\partial V_2}{\partial q}\right)\right] \tag{2.4}$$

$$\boldsymbol{g} = \left(\frac{\partial V_1}{\partial q}\right) - \boldsymbol{h}\left[\left(\frac{\partial V_1}{\partial q}\right) \cdot \boldsymbol{h}\right] \tag{2.5}$$

where $\boldsymbol{h}$ is a normalised vector parallel to $(\partial V_1/\partial q) - (\partial V_2/\partial q)$.

The optimisation can be performed using a simple steepest descent method,[12] to yield results within chemical accuracy. Numerical convergence requires an approximate second-order method such as BFGS Hessian updating.[13]

Knowing the geometry and relative energy of the MECP is frequently enough for a qualitative discussion of the reaction mechanism. An analogous approach is often used for discussing adiabatic reactions: one locates the transition states for the competing pathways, and without performing an RRKM or TST study of the rates, one assumes that the favoured mechanism occurs *via* the lowest TS. Of course, in some cases, dynamical factors may lead to the system preferring to pass through a higher-lying TS, *e.g.* if it is significantly "looser", but by and large the energies already indicate what the mechanism will be. This may be done with MECPs, too, although the rate of passage though these critical points will of course be very low if the coupling between the PESs is exceptionally weak there. Several groups have published studies of spin-forbidden reaction mechanisms in this way.[14,15] More generally, MECPs and the related conical intersections have been used to study other classes of non-adiabatic reactions,[16] including electron transfer processes.[17]

More important in the present context is that knowing the geometry of the MECP provides access to the parameters needed for the non-adiabatic version of RRKM. Thus, as well as the relative energy, the geometry of the MECP also provides, at least within the rigid rotor approximation, its rotational constants. The MECP optimisation also provides the gradients on both PESs at the MECP, and the direction orthogonal to the seam of crossing of the surfaces, which is simply **h**. One can also determine the vibrational frequencies for motion within the seam of crossing around the MECP. The first step is to compute the hessian matrices of second derivatives of each of the PESs with respect to q, H_1 and H_2, at the MECP. One then derives from them the following effective hessian, H_{eff}, for the potential energy of the crossing seam:[11a,12]

$$H_{\mathrm{eff}} = \frac{\left[\left| \frac{\partial V_1}{\partial q} \right| H_2 - \left| \frac{\partial V_2}{\partial q} \right| H_1 \right]}{\left| \frac{\partial V_1}{\partial q} - \frac{\partial V_2}{\partial q} \right|} \tag{2.6}$$

One then multiplies H_{eff} by a projector[18] to remove from it the directions corresponding to the three translational and three rotational degrees of freedom, as well as the direction of, and the resulting a matrix is diagonalised to provide the frequencies.[19] Finally, it is possible to calculate the value of the spin–orbit coupling V_{12} between the two PESs at the MECP using various *ab initio* methods.

With all the required parameters to hand, we have implemented the non-adiabatic RRKM method, using both eqns. (2.2) and (2.3) for the hopping probability, and have applied it to our test case, the decomposition of N_2O, and to the dehydrogenation of CH_3O^+. The densities of states used in eqn. (2.1) were derived within the harmonic approximation, using the steepest descent method.[7a,d] Like the authors of ref. 3*b*, we tested the effects of including some rotational degrees of freedom but they were found to have a negligible effect on the computed rates, so we did not include them in the calculations presented below.

3. Decomposition of N_2O

The dissociation of N_2O to form N_2 and triplet oxygen atom, as well as the related process in which singlet oxygen atoms (O ^{1}D) are non-radiatively converted to the triplet state by collision with diatomic nitrogen, have been the object of a number of experimental and theoretical studies.[20,21] Our aim in the present paper is *not* to improve the quantitative understanding of this reaction, but to compare the predictions of the present simple version of non-adiabatic RRKM theory with those obtained using semi-classical "surface-hopping" trajectory studies, and more sophisticated statistical non-adiabatic theories. We have used the analytical surfaces of ref. 8*c*, which were also used in the studies of refs. 8*e* and *h*. We have also taken the same value of the spin–orbit coupling, *i.e.* 80 cm^{-1}. Using the method described above, we have found the MECP between the two surfaces, which is linear, with $r_{\mathrm{NN}} = 1.105$ Å, and $r_{\mathrm{NO}} = 1.761$ Å, and lies 63.5 kcal mol^{-1} above the N_2O minimum. These results are in reasonable agreement with the data calculated by Chang and Yarkony[20b] for the lowest of the three MECPs, at the MR-CI/TZ2P level ($r_{\mathrm{NN}} = 1.091$ Å, $r_{\mathrm{NO}} = 1.719$ Å, and $E_{\mathrm{rel}} = 59.0$ kcal mol^{-1}). The approximate harmonic frequencies at the MECP are of 132 cm^{-1} (doubly degenerate π bending mode) and 1384 cm^{-1} (N–N stretch).

The microcanonical rate coefficients for dissociation of N_2O calculated using these data, with the two different expressions for p_{sh}, are shown in Fig. 1. Also shown are the predictions of Marks and Thompson[8e] using a Monte-Carlo, phase-space theory (MCPST) method. This is basically a more rigorous version of the non-adiabatic RRKM theory, in that the Monte-Carlo sampling accounts rigorously for the densities of states of eqn. (2.1), which we treat much more crudely within the harmonic approximation. This leads however to a considerable simplification, so that much less information is needed about the PESs. In this case, we used the analytical surfaces to locate the MECP, but in a realistic application, of course, this would be done by *ab initio* computation, as in ref. 20*b*. As can be seen, there is good agreement of our results with those from the more accurate method, suggesting that the harmonic approximation does not fail too badly in this case. Since the MCPST results had been found to reproduce very accurately the results of surface-hopping classical trajectory studies,[8e] the simplicity of the non-adiabatic RRKM approach clearly makes it a useful tool for study of such spin-forbidden rates. We note also that the results are in good qualitative agreement with the predissociation lifetimes (not shown in Fig. 1) computed for over a thousand vibrational eigenstates of singlet N_2O by Nakamura and Kato.[21]

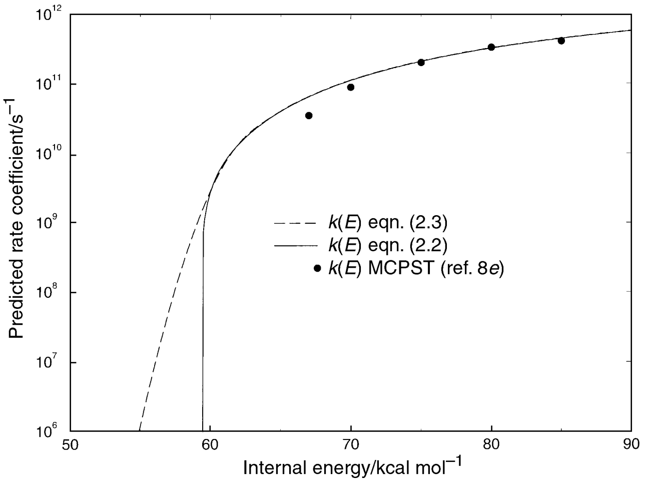

Fig. 1 Predicted rate coefficients for spin-forbidden dissociation of N_2O. Non-adiabatic RRKM results are compared to Monte-Carlo phase-space results obtained on the same PESs in ref. 8*e*.

The predicted rate coefficient rises very sharply when the internal energy reaches the region of the barrier height, then continues to rise more slowly, as discussed *e.g.* in ref. 8*d*. The Landau–Zeener formula of eqn. (2.2) is unable to account for the tunneling behaviour so that the rate coefficient is zero below the barrier. Eqn. (2.3) gives a more correct result, with the coefficient falling off but remaining non-zero even below the barrier. The two formulae lead to excellent agreement for $k(E)$ *above* the barrier, suggesting that their substantial differences[8a] are smoothed over in this case by the averaging involved in eqn. (2.1). Finally, we note that despite using identical potential energy surfaces to Thompson *et al.*, the effective barrier height in the present non-adiabatic RRKM calculations is not the same. This is because the latter include a correction for zero-point vibrational energy (within the harmonic approximation), whereas the CTSH and MCPST calculations do not. There is much less ZPE at the MECP than at the minimum, leading to a corrected MECP height of 59.4 kcal mol^{-1}, almost 4 kcal mol^{-1} below the value on the bare potential. This sort of difference means that quantitative agreement between the predicted rates cannot be expected. Overall, however, the good qualitative agreement between the non-adiabatic RRKM method, which uses only local information on the potential energy surfaces, and the other, much more computationally demanding approaches is very encouraging for the use of this method in applications where only limited *ab initio* data is available.

4. Metastable dehydrogenation of triplet CH_3O^+

The spin-forbidden dehydrogenation of triplet methoxy cation, $^3CH_3O^+$, to form formyl cation, HCO^+, and dihydrogen has been extensively studied using mass-spectrometric and other methods.[1,22] The barrier to dissociation has been found to be very low, since attempts to generate CH_3O^+ directly, by electron ionization (EI) or chemical ionization (CI) of precursor molecules containing methoxy groups lead instead to formyl cation HCO^+, or its ion–molecule complex with dihydrogen, on the time-scale required to isolate the ion. The ion can however be generated, in low yields, by charge-reversal mass spectrometry, starting with the methoxy anion.[22a,b] The partially or fully deuterated species $CH_{3-x}D_xO^+$ ($x = 1$–3) appear to be more stable, so that enough charge-reversal signal is obtained to be able to monitor its unimolecular decay. In all cases, a substantial kinetic energy release (KER) is found, similar to that observed in the unimolecular loss of hydrogen from hydroxymethyl cation. For the mixed deuterated ions ($x = 1$ and 2, above), the kinetic isotopic effects (KIEs) for loss of $H_2/HD/D_2$ have been measured,[1] and the value obtained for CH_2DO^+ has been shown to be incompatible with the measured KIE for dehydrogenation of $CHDOH^+$, if one assumes that the pathway for decay of the former species involves isomerisation to the latter one.

In the paper reporting these KIEs and their analysis, computational data concerning the triplet and singlet PESs of $[C, H_3, O]^+$ was also presented.[1,23] The results are summarised in Fig. 2, with relative energies in kcal mol^{-1} derived from CCSD(T) calculations using the cc-pVTZ basis set,[24] with the d functions on hydrogen omitted, at geometries optimised at the B3LYP/6-311+G(d,p) level, as described in ref. 1. For the MECPs, this level of theory actually refers to geometry optimisation using the hybrid method of ref. 12, using CCSD(T) energies and B3LYP gradients.

As can be seen in Fig. 2, there are two spin-forbidden pathways which can be followed from $^3CH_3O^+$ to give HCO^+ and H_2. The first, "direct", pathway involves motion of two hydrogens towards each other and away from carbon, to lead, after spin inversion, directly to the product channel. The corresponding MECP1 had already been localised in a separate study.[14a] The second, "indirect", route involves motion of one hydrogen atom away from carbon and towards oxygen. After spin change at MECP2, this leads to hydroxymethyl cation CH_2OH^+, which in turn can dissociate adiabatically through a cyclic transition state to give the products. Although the first MECP is lower than the second one, and spin–orbit coupling between the PESs is of the same magnitude at both,[1] the second pathway had long been thought to be the one responsible for dehydrogenation of methoxy cation.[22] In the absence of data concerning the surface crossings, this was really only a hypothesis, based partly on the similarity of the KERDs for dehydrogenation of methoxy and hydroxymethyl cations, and partly on the fact that *ab initio* geometry optimisations on the singlet PES, starting from the triplet minimum geometry, lead to the hydroxymethyl cation minimum.[23]

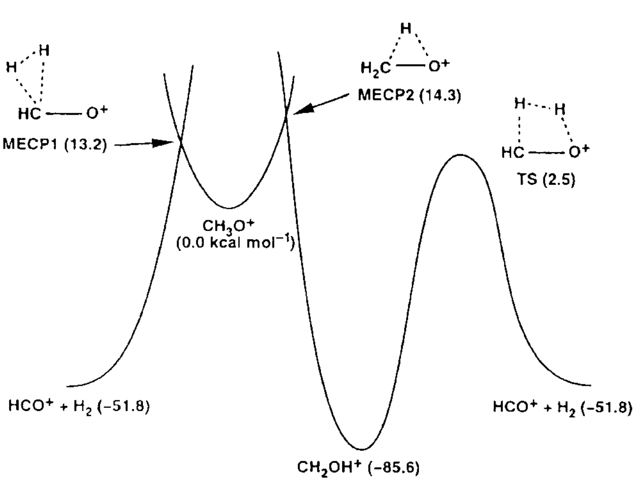

Fig. 2 Schematic singlet and triplet PESs of the $[C, H_3, O]^+$ system, calculated at the CCSD(T)/cc-pVTZ(-d)//B3LYP/6-311+G(d,p) level of theory. Relative energies in kcal mol^{-1}. See ref. 1 for further details.

Combining the experimental and computational evidence, we suggested[1] that the "direct" mechanism was in fact more likely to dominate the reactivity for dehydrogenation of methoxy cation. This was mainly due to the lower MECP energy for that route, and to the inconsistency of the "indirect" route with the observed KIEs. However, using such a qualitative approach, it was not possible to explicitly show that all of the experimental observations were compatible with the suggested mechanism. Thus, we could not directly explain the observed KIEs, nor the greater stability of the deuterated derivatives, nor the similarity of the KERDs for dehydrogenation of methoxy and hydroxymethyl cations. In this article, we use non-adiabatic RRKM predictions of the rate coefficients to examine these points.

The *ab initio* input for the calculations is taken from ref. 1, with CCSD(T)/B3LYP energies as discussed above, B3LYP/6-311+G(d,p) frequencies, and root mean-square values[25] of the singlet–triplet spin–orbit coupling at MECP1 (40.8 cm^{-1}) and MECP2 (45.7 cm^{-1}), derived from FOCI wavefunctions and a semi-empirical one-electron spin–orbit coupling operator. Since our aim is to compare the rates of several competing pathways, we should in principle use a more sophisticated version of eqn. (2.1) to treat the competition between them. However, given the inherently rather low accuracy to be expected from the approach pursued here, we have opted to retain the simplicity of eqn. (2.1) and compute each rate coefficient assuming that the corresponding pathway was the only one which was open from the reactant minimum. We have included a symmetry factor to correct for the different degeneracies of the minimum and the MECPs. Finally, since the energy of both MECPs is well above any remaining barriers to dissociation, we have assumed that the rates for surface crossing at the MECPs can be equated to the rates for dissociation into HCO^+ and H_2.

In Fig. 3, we show the computed rates for surface crossing at MECPs 1 and 2, using the two expressions for p_{sh}. Two trends are clearly visible. First, the rate coefficient for direct dissociation over MECP1 is consistently higher than that for indirect dissociation over MECP2. This confirms our earlier prediction, based on the *ab initio* data alone, that the direct mechanism for dissociation of CH_3O^+ is likely to dominate this reaction. The reason for the higher rate coefficient is almost entirely the lower height of the corresponding MECP. A smaller effect is that frequencies at MECP1 are slightly lower on average than those at MECP2, leading to a slightly increased difference between the ZPE-corrected MECP

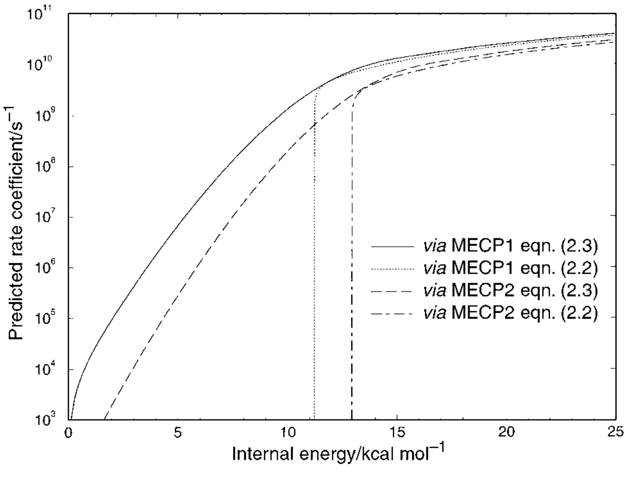

Fig. 3 Predicted rate coefficients for spin-forbidden dissociation of CH_3O^+. Curves are shown for both "direct" (*via* MECP1) and "indirect" (*via* MECP2 and the CH_2OH^+ minimum) dissociation, and are derived using the Landau–Zeener expression [eqn. (2.2)] for the hopping probability, as well as the Airy function-based formula[8a] [eqn. (2.3)].

heights (11.2 and 12.9 kcal mol^{-1} for MECP 1 and 2) with respect to that between the uncorrected values (13.2 and 14.3 kcal mol^{-1}). However, for a given energy above the MECP, this slight difference in the frequencies does not lead to significantly different densities of states at the two MECPs, so that neither pathway is favoured on entropic grounds. As already noted, the spin–orbit coupling between the surfaces is also similar at the two MECPs.

Considering that the difference in the rates is almost entirely due to the small difference in energy of the two MECPs, it could be objected that the prediction is unreliable, because of the expected inaccuracy of the *ab initio* computations. As mentioned in ref. 1, however, we found MECP1 to lie below MECP2 at many different theoretical levels, including CCSD(T) as used here. Given this good agreement of the various methods, the accuracy of the computed *difference* in energy between the two MECPs should be higher than other computed energies, such as the height of each MECP relative to the methoxy minimum, which were found to be more variable from one method to another. As a further check, we recalculated the potential energy surfaces, including the MECPs, using yet another computational method, the highly accurate G3 composite level.[26] For the MECPs, these calculations were performed using the hybrid method of ref. 12, with G3 total electronic energies, including the empirical "higher-level correction", and MP2/6-31G* gradients, as in the G3 method. This leads to energies, without ZPE correction, and relative to the methoxy minimum (total electronic energy: -114.602913), of 13.0 kcal mol^{-1} for MECP1, 14.7 kcal mol^{-1} for MECP2, -85.6 kcal mol^{-1} for hydroxymethyl cation, 3.0 kcal mol^{-1} for the adiabatic TS for loss of H_2 from this ion, and -51.2 kcal mol^{-1} for the products, formyl cation and dihydrogen. These results are very close to the CCSD(T) values of Fig. 2 and ref. 1, lending further support to the calculated PESs, and especially to the fact that MECP1 lies lower than MECP2—we note that the difference is 1.7 kcal mol^{-1} at the G3 level, as against 1.1 kcal at the CCSD(T) level used for the RRKM calculations in this paper, suggesting that the rate coefficient differential between direct and indirect routes is if anything larger than that predicted here.

A second noticeable trend is that the rates for both pathways are exceedingly high for energies above the barrier. Below the barrier, the rates computed using the Landau–Zeener expression [eqn. (2.2)] are zero, but those given by eqn. (2.3) remain rather large even down to very low energies. The experimental metastable decomposition occurs on the ms timescale, corresponding to rate coefficients of the order of 10^5–10^6 s^{-1}, and it can be seen in Fig. 3 that the internal energy of ions predicted to decompose on this timescale is well below the energy of the MECP. This accounts for the many difficulties which befell experimental attempts to make the ion, since it can be seen that even very moderate amounts of internal energy will lead to decomposition. At energies well below the threshold, the accuracy of the method is questionable, however, so that quantitative predictions concerning, *e.g.*, the stability of the rovibrationally coldest ions, should not be expected.

In Fig. 4, we show total decomposition rates for the four isotopic variants of $CH_{3-x}D_xO^+$ ($x = 0$–3), considering the "direct" channel *via* MECP1 only, and using only the rates derived from the Delos expression [eqn. (2.3)] for the surface-hopping probability. For the mixed compounds ($x = 1$ or 2), the rates shown are the sum of the rates for loss of H_2, HD and D_2. As can be seen, the rate coefficient for decomposition is predicted to be lower the more deuterium atoms are present. If one assumes that the charge-reversal process leads to similar amounts of internal energy deposition in all the nascent methoxy cations, this would explain why the experimental yield of methoxy cations with lifetimes long enough to be monitored is higher for the deuterated cations. As above, one should however underline the hazardous nature of quantitative predictions in this below-threshold regime.

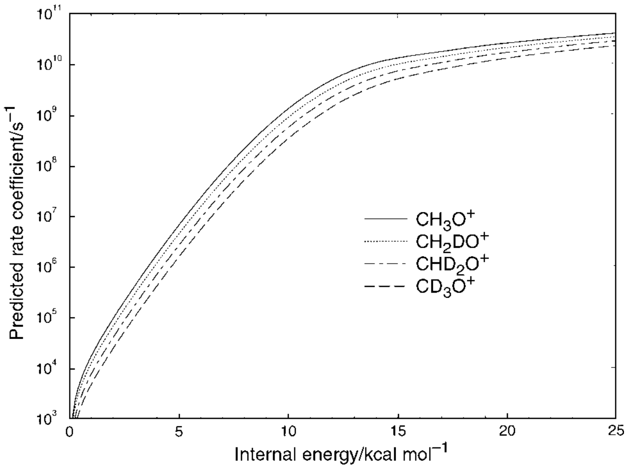

Fig. 4 Total dissociation rate coefficients as a function of internal energy for loss of H_2, HD or D_2 from triplet $CH_{3-x}D_xO^+$ ions. The rates for the mixed species ($x = 1$, 2) are obtained by summing the rates for loss of HD and H_2 or D_2, respectively.

Finally, in Fig. 5, we show predicted rate coefficients for loss of HD and of D_2 from CHD_2O^+. As can be seen, the former rate coefficient is predicted to be larger in all energy ranges, by about a factor of 4 to 5 in the range of energies corresponding to metastable decomposition on the μs timescale. However, since there are two ways of losing HD, and only one for losing D_2, this corresponds to a kinetic isotope effect of *ca.* 2 only. In the present calculations, this KIE can be attributed to ZPE effects. Thus, upon going from the methoxy minimum to MECP1, two of the stiff C–H stretching modes are lost, whereas the H–H stretching mode is not yet present. There is thus less ZPE at the MECP1 than at the minimum, for all isotopic substitution patterns. In the partially deuterated cases, however, the difference is greatest when it is the C–H bonds which are broken at the MECP. Thus, there is less ZPE at the $DCO^+(HD)$ MECP1, which leads to HD loss, than at the corresponding $HCO^+(D_2)$ MECP1, for loss of D_2. Since the starting point is the same in both cases, this leads to different thresholds, of respectively 11.4 and 11.8 kcal mol^{-1} for loss of HD and D_2, accounting for the higher rate coefficient associated with the former pathway.

The experimental[1] KIE is of 10 ± 2, so that although it is encouraging that our predictions show that there *is* a KIE, they fall considerably short of the observed value. The same trend is obtained for the loss of H_2 and HD from CH_2DO^+,

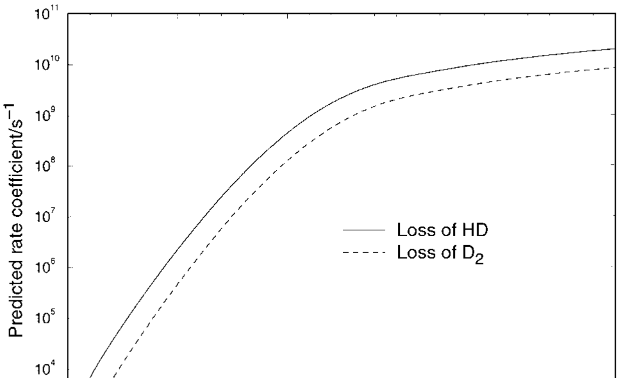

Fig. 5 Predicted dissociation rate coefficients for loss of HD or D_2 from CHD_2O^+ ion.

where a KIE of *ca.* 2 is predicted, as compared to the experimental value of 8. These discrepancies can partly be explained by the expected low accuracy of the predicted rates in the tunnelling regime, due to failure of eqn. (2.3) and its assumptions. But beyond this general point, the separability assumption of the non-adiabatic RRKM method probably fails also, strongly contributing to the discrepancy. This assumption considers that the motion in the "hopping" direction, orthogonal to the seam, takes place independently of the "harmonic bath" motions, which are parallel to the seam. The tunnelling behaviour therefore occurs strictly along the "hopping" coordinate, and is subject to the reduced mass of that direction. In the case of CH_2DO^+, the effective mass for motion across the seam at MECP1 is rather large in both isotopic variants of the MECP, being equal to 10.33 and 10.43 u, respectively, for loss of H_2 and HD. These large values reflect the fact that as one goes from CH_3O^+ to $HCO^+ + H_2$, although the most apparent motion is that of the hydrogen atoms, there is also a large change in the C–O bond length, which goes from a single bond in CH_3O^+ (1.295 Å at the B3LYP/6-311+G(d,p) level of theory) to a triple bond in HCO^+ (1.103 Å). The direction orthogonal to the seam reflects this fact, in that it contains a sizeable contribution corresponding to contraction of the C–O bond, thus leading to large effective masses.

In reality, the surface-hopping in the tunnelling regime is expected to be dominated by motions of the lighter hydrogen atoms alone. Given the C–H bond breaking and H–H bond formation which occur in going from CH_3O^+ to $HCO^+ + H_2$, these motions in fact already make up a considerable part of the hopping coordinate. But one can expect that the tunnelling will occur along a direction made up *only* of hydrogen atom motions, with the C–O moiety frozen. In turn, because it is mostly the departing hydrogens which move, the tunnelling should be stronger at the $DCO^+(H_2)$ MECP1 than at the corresponding $HCO^+(HD)$ arrangement, thus accounting for the high experimental H_2/HD KIE.

This behaviour can also be described as involving crossing the seam along a pathway which is not orthogonal to it, or as a coupling between the motion in the "hopping" coordinate and the "harmonic bath" coordinates. This last description highlights why the separability assumption precludes the inclusion of such behaviour within the non-adiabatic RRKM picture.

5. Non-adiabatic RRKM: discussion

As shown above in Sections 3 and 4, the non-adiabatic RRKM method, with input from *ab initio* computations, leads to qualitatively useful and accurate predictions of the microcanonical rate coefficients for two sample spin-forbidden unimolecular decay reactions. Thus, for the decomposition of N_2O to N_2 and $O(^3P)$, the predicted rate coefficients are in very good agreement with results obtained on the same potential energy surfaces, but using much more computationally demanding theoretical methods. For the loss of hydrogen from methoxy cation, the predictions are in good agreement with the experimental results.

Given these successes, even the rather simple non-adiabatic RRKM expression for spin-forbidden rate coefficients used here should be useful in many other cases for the semiquantitative modelling of reaction rates. However, as it is subject to all the approximations of RRKM theory,[7] and to some supplementary ones of its own, it can be expected to have all the corresponding failings. It is useful to briefly enumerate these.

(i) First, the method is dependent on obtaining good information on the PESs, which in most cases will involve performing reliable *ab initio* computations. Just as it is crucial in normal RRKM to correctly predict the relative energy of the transition state, it will be important to find the height of the MECP at a sufficiently good level of theory. As discussed in ref. 12, an additional difficulty for MECPs compared to TSs is that it is not possible to use high-level single-point computations at an MECP geometry optimised at a lower level. This difficulty has also been discussed by others, who have found that there is sometimes a considerable difference between the energies of the two PESs concerned upon performing single-point calculations at one level at an MECP geometry optimised at another level.[9,14b] It is for this reason that we introduced the hybrid method of ref. 12 for locating MECPs using energies computed at one level, and gradients at another. This hybrid method has proven invaluable for the present system, enabling us to determine the height of the MECP at the CCSD(T) and G3 levels of theory.

(ii) As in RRKM, various approximations need to be made for calculating the densities of states. Typically, one needs to assume that the modes within the crossing seam can be treated as uncoupled harmonic oscillators, and that the MECP can be treated as a rigid rotor. This approximation has been extensively discussed in the context of RRKM and TST,[7] and we will simply mention that whilst it is possible to go beyond it, this generally requires a very considerable increase in computational expense, and a much extended amount of information concerning the potential energy surface.[27]

(iii) As discussed above, the assumption of separability between the modes is probably the reason why our results for the KIE for loss of HD or D_2 from CHD_2O^+ are not in quantitative agreement with experiment. This assumption is problematic for all statistical rate theories, and although approximate methods have been suggested to account for multi-dimensional tunnelling behaviour,[28] they require considerably more information about the PES than ordinary methods, and have not yet been extended to non-adiabatic reactions.

(iv) In some situations, non-ergodicity may be a problem, as for ordinary statistical rate theories.

(v) Although re-hopping from the product PES back to the reactant one is not expected to be as significant as transition state recrossing in adiabatic theories, it will clearly occur more frequently for systems with substantial spin–orbit coupling, especially if there are dynamical bottlenecks hindering the motion of the system away from the crossing seam on the product PES.

(iv) Eqns. (2.2) and (2.3) both assume a constant value for the spin–orbit coupling between the PESs in the region where hopping is supposed to take place, around the MECP. In cases where, for example, the spin density on different atoms changes significantly around the crossing seam, this is not a good approximation. As an example, in the reactions of oxygen atoms with halide-containing compounds,[14b,29] the unpaired electrons in the triplet state are both mainly located on oxygen in some regions of the PES, but in others, they are spread over oxygen and the halogen. Given the larger intrinsic spin–orbit coupling constants of the heavy halogens, this will lead to different values of the spin–orbit coupling in these different regions. It is possible to account partly for such effects by calculating the SOC matrix element along the hopping coordinate, and using it in a numerical, one-dimensionally "exact", treatment of the hopping probability instead of the simpler eqns. (2.2) or (2.3).[9a,30] Possible extensions to treat the variation of the SOC along the other coordinates have also been discussed.[9a] Such approaches should lead to slight increases in accuracy. However, they require much more information on the PESs than the simple approach, and, considering the many other inaccuracies of the non-adiabatic RRKM approach, probably do not lead to substantially better predictions in many cases.

(vii) Eqns. (2.2) and (2.3) for the hopping probability are based on calculating the overlap between one-dimensional reactant and product free particle-like wavepackets on linear potentials. In cases where the nuclear wavefunctions of either the reactant or the product differ significantly from this model, the hopping probability will be wrong. An important example is for systems where the MECP lies very low in energy above the reactant minimum, so that the nuclear wavefunction will resemble a ground state harmonic eigenfunction. Thus, for systems such as spin isomerisation of triplet phenyl cation[12] or predissociation of OCCO,[15e] a high accuracy cannot be expected from the non-adiabatic RRKM approach. In general cases, however, the extensive averaging involved in eqn. (2.1) will compensate for errors in eqns. (2.2) and (2.3), since these will by and large predict the right order of magnitude for the hopping probability, but will get it too large for some energies and too small for others. A more serious problem with deriving the hopping probability from a free particle model is that one assumes a continuous density of states across the whole spectrum of hopping coordinate energies. In many cases, the density of states will be high enough in at least one of the states, so that the averaging will again compensate for this. However, in some small systems, such as the spin isomerisation of singlet and triplet CH_2, the mismatch between the energies of the reactant and product eigenfunctions will be such as to lead to a negligibly low isomerisation rate.[31]

6. Classical trajectory simulation of KERs

As mentioned in Section 4, it has been observed that the KERDs upon metastable decay of CH_2OH^+ and CH_3O^+ to form HCO^+ and H_2 are very similar.[1,22] This has been used as an argument supporting the occurrence of the "indirect" mechanism, *via* hydroxymethyl cation, during the dissociation of methoxy cation.[22b] Our previous *ab initio* results[1] and present RRKM study support instead the "direct" mechanism, suggesting that the similarity of the KERDs is in fact accidental. To test this hypothesis, we have attempted to predict the KERD for metastable dissociation of CH_2OH^+ and of CH_3O^+. Whilst statistical methods for predicting partitioning of energy in unimolecular decomposition products are available,[7d] these methods have mostly been developed for adiabatic decay processes and are thus not directly applicable to the "direct" dissociation pathway. Instead, we have chosen to compute the KERDs from quasi-classical trajectory calculations starting from the transition state for hydrogen elimination from CH_2OH^+, and from MECP1 for "direct" elimination of H_2 from CH_3O^+. Although an analytical potential energy surface has been developed for the CH_2OH^+ system, and indeed used in quasi-classical trajectory studies of its decomposition,[32] it is not clear whether this potential surface describes adequately the region of MECP1. Therefore, we chose instead to integrate the classical trajectories using HF/6-31G** *ab initio* computations "on the fly", that is, the potential and forces were computed at this level of theory at each time step during the propagation.

These *ab initio* calculations were performed using the Gamess-USA program.[33] The integration was performed using a velocity Verlet algorithm[34] with a time step of 0.15 or 0.20 fs, until the two products were separated by more than 5 Å. Initial conditions were selected as follows. For the adiabatic TS, the Hessian was computed and diagonalised, to yield the frequencies and eigenvectors. Then, a kinetic energy of 0.05 kcal mol^{-1} was given to the system in the direction of the imaginary mode, and with the velocity oriented towards the products. Each of the $3N$–7 transverse modes were given random initial displacements and velocities according to the Wigner distribution[35] of the corresponding ground state harmonic oscillator wavefunction. For the trajectories starting at MECP1, the geometry of that MECP was first optimised using the hybrid method of ref. 12, with HF/6-31G** gradients and MP2/6-311+G(d,p) energies. This leads to a geometry and energy (relative to the methoxy minimum and the adiabatic TS) close to the "best" results of ref. 1. Thus, the HF/6-31G** singlet energy at that geometry is 8.1 kcal mol^{-1} higher than at the adiabatic TS at the same level, compared to a difference of 10.7 kcal mol^{-1} obtained at the CCSD(T) level in ref. 1. At this geometry, the effective Hessian of eqn. (2.6) was then computed and diagonalised, to give frequencies and eigenvectors for the transverse modes within the seam of crossing. These were then used to generate initial displacements and velocities according to the Wigner distribution of the corresponding ground state harmonic oscillator wavefunction. 400 trajectories each were run from the MECP and the TS.[36] We note that an *ab initio* direct dynamics study of this reaction, also at the HF level of theory with a polarised basis set, has already been performed.[37] Due to computational restrictions, however, only one trajectory, initiated at the saddle point, was run for each isotopomer considered.

In contrast, our approach, described above, is designed to select an ensemble of initial conditions to provide an adequate quasi-classical representation of the "zero-point" levels of MECP1 and of the H_2-elimination TS, with a negligible kinetic energy along the unique mode (the mode orthogonal to the seam or the imaginary mode, respectively), that is, of near-threshold systems. In fact, our present non-adiabatic RRKM study, together with the previous adiabatic RRKM study[38] of dehydrogenation of CH_2OH^+, has shown that reactivity in these systems on the μs-metastable decay timescale is dominated by *below*-threshold contributions. These cannot, however, be meaningfully simulated using quasi-classical trajectories. We also note that although it gives a better representation of the quantum zero-point energy in the transverse modes, the Wigner distribution does not yield a microcanonical ensemble of quasi-classical initial conditions, unlike some other methods for selecting initial conditions.[39] In fact, our incorrect use of normal mode harmonic oscillator wavefunctions in the Wigner distribution potential further broadens the spread of the total energies.

The results are shown in Fig. 6. As can be seen, the distribution of translational energy observed is very similar from the MECP and from the TS, confirming the above hypothesis. In both cases, the KERD is in fact displaced to higher energies compared to the experimental distribution. Thus, the average KER obtained from the trajectories initiated at the TS is of 55.1 kcal mol^{-1}, compared to 37.6 kcal mol^{-1} experimentally.[32] This is because both MECP1 and the TS lie higher with respect to the products, HCO^+ and H_2, at the HF/6-31G** level than they do at higher levels of theory, which are in agreement on this point with experiment. Thus, MECP1

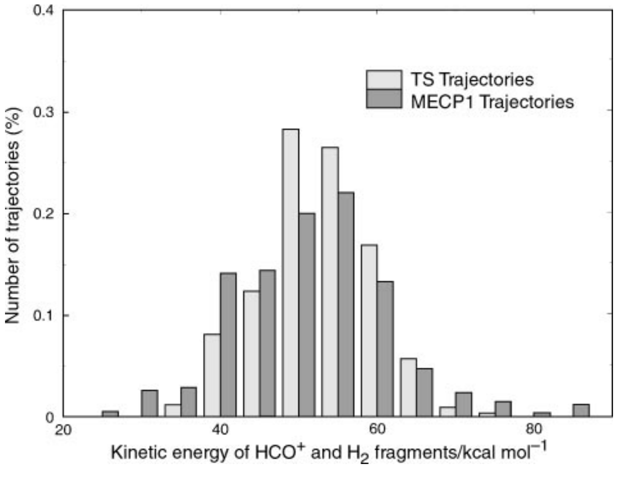

Fig. 6 Kinetic energy release distribution from HF/6-31G** *ab initio* classical trajectories initiated at the adiabatic TS for decomposition of CH_2OH^+ and at the "direct" MECP1 for spin-forbidden dissociation of CH_3O^+.

and the TS lie respectively 73.9 and 65.8 kcal mol^{-1} above the products at the HF/6-31G** level, compared to 65.0 and 54.3 kcal mol^{-1}, respectively, at the CCSD(T) level of ref. 1. It is therefore more meaningful to express the average KER as a percentage of the barrier height, leading to a value of 84% for our calculated results, and 75% experimentally, in better agreement. A similar situation was found in a study of the dissociation of formaldehyde to CO and H_2 by "on the fly" integration of classical trajectories using *ab initio* computation of the potential and its derivatives.[40] Thus, at the levels of theory used for the trajectory calculations (HF/3-21G and HF/6-31G**), the barrier to dissociation was found to be too high as compared to experiment and better calculations. As in our case, this led to computed kinetic energy releases which were much higher than those experimentally observed.

7. Conclusions

In this paper, we have set out to compare theory with experiment for the spin-forbidden dissociation of triplet methoxy cation. To do so, we have applied a previously developed[3] non-adiabatic RRKM theory to predict the rates of various spin-forbidden reactions of CH_3O^+ and its isotopomers. We have also shown that all the parameters needed for this theory can be rigorously derived from *ab initio* calculations. The predictions are in good agreement with experiment.[1]

(i) The "direct" loss of H_2 is predicted to take place faster than the "indirect" loss, occurring *via* hydroxymethyl cation. Experiments have shown that observed product ratios are not compatible, with the "indirect" mechanism being the dominant one.

(ii) The ions are predicted to decay on a µs timescale, even for rather low internal energies. Among the isotopic variants, decomposition is predicted to be fastest for CH_3O^+, and slowest for CD_3O^+. Experimentally, the cations have proved very difficult to make, because they undergo decomposition before they can be identified, using most methods. Even with the "softest" method for generation, charge reversal from the anion, which is expected to lead to cations with little internal energy, due to the similar geometries of the anion and the cation, the cation decomposes rapidly on the µs timescale, leading to low charge-reversal yields. The highest yields are obtained for CD_3O^+, the lowest for CH_3O^+.

(iii) The loss of HD is predicted to be faster than that of D_2 from CHD_2O^+ ions. This is also observed experimentally.

This good agreement, coupled with the fact that the theory only requires *local* information on the PESs involved, and thus a limited number of *ab initio* computations, should make non-adiabatic RRKM very attractive for applications to other polyatomic systems and we are pursuing work in this direction.

Finally, as a further comparison with experiment, a classical trajectory study of the kinetic energy release distribution of methoxy dissociation has been performed, using "on the fly" *ab initio* calculations to determine the potential and gradient on the singlet $[C, H_3, O]^+$ PES. This study has confirmed that the KERD from direct dissociation of triplet methoxy cation and that from adiabatic decomposition of singlet hydroxymethyl cation should be very similar. The observed similarity of the KERD for dissociation of methoxy and hydroxymethyl cations[22b] does not, therefore, provide support for the intermediacy of hydroxymethyl cation in the dissociation of methoxy cation.

8. Acknowledgements

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