Theoretical Treatment of Magnetic Field Dependent In-cage Backward Electron Transfer During Photooxidation of Ru(II) Complexes

By Ulrich E. Steiner and Dieter Brner

Fakultt fr Chemie, Universitt Konstanz, D-7750 Konstanz,
Federal Republic of Germany

(Received October 31, 1990)

Magnetokinetic theory / Spin-orbit coupling / Photoelectron transfer

A theoretical treatment is presented of the magnetic field dependence of in-cage backward electron transfer within the primary redox pair originating from electron transfer between photoexcited Ru(II)-trisbipyridyl $[\text{Ru}(\text{bpy})_3^{2+}]$ and methylviologen (MV^{2+}). The treatment is based on the numerical solution of a stochastic Liouville equation for a density matrix represented in the basis of an explicitly given set of spin-orbit states of the redox pair $[\text{Ru}(\text{bpy})_3^{3+} \dots \text{MV}^+]$. Calculations with various sets of model parameter values were performed in order to obtain the best fit to the experimentally observed magnetic field dependence of the efficiency of cage escape. A reasonable simulation required the assumption of substantial initial singlet character of the primary redox pair and a very high rate of relaxation within the set of its four lowest spin-orbit states. A rate constant of about 10^{11} s^{-1} for a hypothetically spin-allowed backward electron transfer was evaluated.

Die Magnetfeldabhngigkeit des ,in-cage' Rckelektronentransfers im primren Redoxpaar, das sich beim Elektronentransfer von photochemisch angeregtem Ru(II)-trisbipyridin $[\text{Ru}(\text{bpy})_3^{2+}]$ auf Methylviologen (MV^{2+}) bildet, wird theoretisch behandelt. Der Formalismus grndet sich auf die numerische Lsung einer stochastischen Liouville-Gleichung fr die Dichtematrix des Redoxpaares $[\text{Ru}(\text{bpy})_3^{3+} \dots \text{MV}^+]$, die in der Basis eines Satzes von explizit angegebenen Spin-Bahn-Zustnden dargestellt wird. Um die beste Anpassung der experimentell bestimmten Magnetfeldabhngigkeit der ,cage-escape' Effizienz zu erhalten, wurden Berechnungen mit verschiedenen Stzen von Modellparametern durchgefhrt. Fr eine befriedigende Simulation der Magnetfeldabhngigkeit mu von einem betrchtlichen Singlett-Anteil im primr gebildeten Redoxpaar und von sehr schnellen Relaxationsbergngen zwischen den 4 niedrigsten Spin-Bahn-Zustnden des Redoxpaares ausgegangen werden. Die Ratenkonstante fr den hypothetisch spin-erlaubten Elektronenrcktransfer im Redoxpaar wurde zu etwa 10^{11} s^{-1} ermittelt.

1. Introduction

A considerable variety of magnetic field dependent reaction kinetics has been described during the last 20 years, and the analysis of such magnetokinetic effects has provided a wealth of valuable information on elementary reaction steps connected to the chemical behaviour of reaction intermediates with weakly coupled pairs of electron spins [1]. Recently, magnetic field effects (MFEs) on the yield of electron transfer products in the photooxidation of Ru-trisbipyridyl complexes were reported for the first time [2, 3]. According to experiments in this laboratory, significant MFEs on the lifetime of the photoreactive Ru-complex do not occur either in the absence or in the presence of the electron acceptor (methylviologen) in the field range investigated of 0–3 T [3, 4]. Therefore it was concluded [3] that the MFE must arise in the primary redox pair (RP) *after* the photoinduced forward electron transfer step.

The following scheme is generally adopted to account for net electron transfer efficiencies smaller than one.

Scheme I

Diffusional separation of the RuL_3^{3+} and the $\text{MV}^{\cdot+}$ ions occurring with a rate constant k_{ce} (ce = cage escape) has to compete with backward electron transfer occurring with an effective rate constant $\bar{k}_{bet}$, so that the net efficiency of free redox product formation may be described as an efficiency of cage escape, η_{ce} [5].

$$\eta_{ce} = \frac{k_{ce}}{k_{ce} + \bar{k}_{bet}} \quad (1)$$

It is generally accepted that the photoreactive state of the Ru-complex is a ${}^3\text{MLCT}$ state, although some disagreement exists with regard to the singlet contamination of this state (or group of states separated by several cm^{-1}) [6–12]. In Scheme I the possibility of spin-mixed character is indicated by the symbol 3 . As we have pointed out [3] the in-cage backward electron transfer leading to singlet ground state products should be subject to spin restrictions, since the primary RP should originate with the same overall spin as the encounter pair. We have outlined how the MFE on the effective rate of backward electron transfer should be dealt with theoretically. The pertinent magnetokinetic mechanism that is controlled by the effect of spin-

orbit coupling (SOC) at the Ru(III)-center exhibits features of both the Δg -type radical pair mechanism (cf. Ref. 1) and the triplet mechanism [13, 14]. However, the present situation requires a special theoretical treatment owing to the participation of a strongly spin-orbit mixed Kramers doublet species (RuL_3^{3+}) in the RP. In this paper we will present a formally consistent theoretical model and its numerical evaluation, applied to the experimental data on the MFE described above.

2. Theory

2.1. Spin-orbit states of the redox pair ($\text{RuL}_3^{3+} \dots \text{MV}^\pm$)

The effective spin states of the RP may be represented in the direct product basis of two doublets, whereby the $\text{MV}^\pm$ radical is represented by a normal spin doublet, but the Ru(III)L_3 moiety by a strongly spin-orbit coupled Kramers doublet.

To describe the electronic state of the Ru(III) core in a trigonally distorted octahedral ligand field we will use the coordinate system depicted in Figure 1. Using the real d -orbitals

$$d_{yz} = \sqrt{\frac{15}{4\pi}} \frac{yz}{r^2}, \quad d_{xz} = \sqrt{\frac{15}{4\pi}} \frac{xz}{r^2}, \quad d_{xy} = \sqrt{\frac{15}{4\pi}} \frac{xy}{r^2}, \quad (2a-c)$$

$$d_{z^2} = \sqrt{\frac{5}{16\pi}} \frac{2z^2 - x^2 - y^2}{r^2}, \quad d_{x^2-y^2} = \sqrt{\frac{15}{16\pi}} \frac{x^2 - y^2}{r^2}, \quad (2d, e)$$

the three lowest d -orbitals of D_3 -symmetry correlating with the t_{2g} -set of octahedral symmetry may be expressed as

$$a_1 = d_{z^2}, \quad (3a)$$

$$e_\pm = \frac{1}{\sqrt{3}} \left(-\frac{1}{\sqrt{2}} d_{yz} \mp \frac{1}{\sqrt{2}} d_{xz} \pm d_{xy} + i d_{x^2-y^2} \right). \quad (3b)$$

The following normalized Slater determinants will be used as basis states to describe the lowest Kramers doublet of the Ru(III) complex. The phases are chosen in such a way as to achieve correspondence with the functions used by Hipps and Crosby [6], whose notation is given by the $| \rangle$ symbols.

$$|a_1| \equiv |e_+ \bar{e}_+ e_- \bar{e}_- a_1| = |1E'\alpha'\rangle \quad (4a)$$

$$|\bar{a}_1| \equiv |e_+ \bar{e}_+ e_- \bar{e}_- \bar{a}_1| = |1E'\beta'\rangle \quad (4b)$$

$$|\bar{e}_-| \equiv -|e_+ \bar{e}_+ \bar{e}_- a_1 \bar{a}_1| = |2E'\alpha'\rangle \quad (4c)$$

$$|e_+| \equiv -|e_+ e_- \bar{e}_- a_1 \bar{a}_1| = |2E'\beta'\rangle. \quad (4d)$$

The shorthand notation chosen for the Slater determinants indicates the spin state of the unpaired electron. The lowest Kramers doublet of a Ru(III) complex of D_3 symmetry may be expressed in the general form

$$\alpha' = \sin(x)|a_1| + \cos(x)|\bar{e}_-| \quad (5a)$$

$$\beta' = \sin(x)|\bar{a}_1| + \cos(x)|e_+|. \quad (5b)$$

The extent of mixing of different spin-orbital states expressed by the angle x is determined by the ratio of the trigonal ligand field splitting parameter Δ (positive if $|a_1|$, $|\bar{a}_1|$ are lower in energy than $|e_+|$, $|\bar{e}_-|$) and the one-electron SOC constant ζ of the Ru 4d shell. The pertinent relation is [15–17]

$$\tan(2x) = \frac{\sqrt{2}}{1/2 - \Delta/\zeta} \quad (6)$$

with $0 \leq 2x \leq \pi$.

The ratio Δ/ζ can be determined experimentally from the g -tensor components of the Ru(III) complex.

Combining the components α' and β' of the lowest Kramers doublet of the Ru(III) complex with the normal spin doublet (α, β) of the MV^+ radical, the RP states may be represented in the direct product basis:

$$|\alpha'\alpha\rangle, |\alpha'\beta\rangle, |\beta'\alpha\rangle, |\beta'\beta\rangle. \quad (7)$$

In order to analyse for the contributions of pure spin states to the energy eigenstates of the radical pair, we use the following basis of pure spin states for the Ru(III)/ MV^+ pair:

$$T_+(a_1r) = ||a_1|r| \quad (8a)$$

$$T_-(a_1r) = ||\bar{a}_1|r| \quad (8b)$$

$$T_0(a_1r) = 1/\sqrt{2} (||a_1|\bar{r}| + ||\bar{a}_1|r|) \quad (8c)$$

$$S_0(a_1r) = 1/\sqrt{2} (||a_1|\bar{r}| - ||\bar{a}_1|r|). \quad (8d)$$

Here the symbol (a_1r) specifies the configuration by noting the singly occupied molecular orbitals, r standing for the SOMO orbital in MV^+ . The symbol $||a_1|r|$ is a shorthand notation for a compound six-electron Slater determinant, for example:

$$||a_1|r| \equiv |e_+ \bar{e}_+ e_- \bar{e}_- a_1 r|. \quad (9)$$

Definitions analogous to those given in Eqs. (8) are used for the four spin states corresponding to the configurations $(e_\pm r)$. Altogether these functions represent a basis of twelve pure-spin RP states. From the product states (7) we can construct the formal equivalents $T'_\pm$, T'_0 , S' to the RP spin

eigenstates $T_{\pm}$, T_0 , S which are normally used in the theory of the radical pair mechanism.

$$T'_+ \equiv |\alpha'\alpha\rangle = \sin(x) T_+(a_1r) + 1/\sqrt{2} \cos(x) [T_0(e-r) - S(e-r)] \quad (10a)$$

$$T'_- \equiv |\beta'\beta\rangle = \sin(x) T_+(a_1r) + 1/\sqrt{2} \cos(x) [T_0(e+r) - S(e+r)] \quad (10b)$$

$$T'_0 \equiv 1/\sqrt{2} (|\alpha'\beta\rangle + |\beta'\alpha\rangle) \\ = \sin(x) T_0(a_1r) + 1/\sqrt{2} \cos(x) [T_+(e+r) - T_-(e-r)] \quad (10c)$$

$$S' \equiv 1/\sqrt{2} (|\alpha'\beta\rangle - |\beta'\alpha\rangle) \\ = \sin(x) S(a_1r) + 1/\sqrt{2} \cos(x) [T_+(e+r) - T_-(e-r)]. \quad (10d)$$

The primed symbols used for the pair spin states refer to a formal or effective spin, quantized along the C_3 axis of the Ru complex. If one replaced the MV^+ localized orbital r by the lowest ligand π^* orbital, our primed RP spin states, in the order given in Eqs. (10), would correspond to the state functions $|E_+\rangle$, $|E_-\rangle$, $|A_1\rangle$, $-|A_2\rangle$ introduced by Hipps and Crosby [6] to describe the lowest group of MLCT states of $Ru(bpy)_3^{2+}$ [18]. In the excited $Ru(bpy)_3^{2+}$ complex these states are split by some ten wavenumbers [11, 12, 19, 20]. In the redox pair state in which the r orbital is not on a ligand but on the electron acceptor MV^{2+} , the four states will be assumed as approximately degenerate. It must be noted, though, that a residual splitting due to exchange interaction at the separation of the RP in contact, might modify the resulting magnetic field dependence of RP dynamics (cf. Discussion).

In our representation (Eq. 10) the true spin origin of the RP states can be recognized. It becomes clear that, except for T'_0 which is a pure $S = 1$ state, all RP states are considerably singlet-contaminated. From this we may conclude, that after formation of the RP, there will be a strong tendency of fast backward electron transfer for the formal spin states T'_+ , T'_- and S' , whereas the formal spin state T'_0 cannot undergo direct backward electron transfer. From the RPs in T'_0 , formation of escape radicals will be the dominant process. However, the absolute yield of escape radicals will depend on possible transitions from T'_0 to S' or $T'_{\pm}$ during the cage lifetime of the RP. In the following, we will show that such transitions can be brought about by an external magnetic field, but also by the rotational motion of the $Ru(III)$ complex.

2.2. Zeeman mixing of radical pair spin states

We consider the following spin Hamilton operator

$$H = -\mu_B B_0 A, \quad (11)$$

where the vector operator A is given by

$$A = g_{Ru} S_{Ru} + g_{MV} S_{MV}. \quad (12)$$

Here S_{Ru} and S_{MV} are effective spin operators for the Ru complex and the MV^+ radical, respectively. The g -tensor of the Ru complex is strongly anisotropic [25]. Consistent with our representation of the Kramers doublet (Eqs. 2–5), are the following expressions:

$$g_{\parallel} = g_{zz} = 2[\sin^2(x) - (1 + k)\cos^2(x)] \quad (13a)$$

$$g_{\perp} = g_{xx} = g_{yy} = 2[\sqrt{2}k\sin(x)\cos(x) + \sin^2(x)]. \quad (13b)$$

Here k is the orbital dilution factor.

The g -factor of MV^+ is very close to that of a free electron [21]. It will be considered as isotropic, the subscript MV being omitted. In the basis of states T'_+ , T'_- , T'_0 and S' the matrices of the vector components of the operator A can be expressed as:

$$\begin{array}{c} \text{basis states:} \quad T'_+ \quad T'_- \quad T'_0 \quad S' \\ A_x = \frac{1}{2\sqrt{2}} \begin{pmatrix} 0 & 0 & (g_{xx} + g) & -(g_{xx} - g) \\ 0 & 0 & (g_{xx} + g) & (g_{xx} - g) \\ (g_{xx} + g) & (g_{xx} + g) & 0 & 0 \\ -(g_{xx} - g) & (g_{xx} - g) & 0 & 0 \end{pmatrix} \end{array} \quad (14a)$$

$$A_y = \frac{i}{2\sqrt{2}} \begin{pmatrix} 0 & 0 & -(g_{yy} + g) & (g_{yy} - g) \\ 0 & 0 & (g_{yy} + g) & (g_{yy} - g) \\ (g_{yy} + g) & -(g_{yy} + g) & 0 & 0 \\ -(g_{yy} - g) & -(g_{yy} - g) & 0 & 0 \end{pmatrix} \quad (14b)$$

$$A_z = \frac{1}{2} \begin{pmatrix} (g_{zz} + g) & 0 & 0 & 0 \\ 0 & -(g_{zz} + g) & 0 & 0 \\ 0 & 0 & 0 & (g_{zz} - g) \\ 0 & 0 & (g_{zz} - g) & 0 \end{pmatrix} \quad (14c)$$

These matrices represent the couplings exhibited by the respective components of the magnetic field along the axes x , y , and z of the Ru(III) complex. From the representation of A_z we see that a magnetic field along the C_3 axis of the complex mixes T'_0 with S' . This mixing corresponds to the familiar Δg -mechanism of magnetic field dependent radical pair reactions. From the representation of A_x and A_y , magnetic field components perpendicular to the C_3 axis of the complex are seen to mix T'_0 with T'_+ and T'_- . As shown in Eqs. (10), the latter are singlet-contaminated and

Fig. 1. Definition of coordinates (x, y, z) used for describing spin-orbital wavefunctions and molecular rotation of the $\text{Ru}(\text{bpy})_3^+$ complex. The nitrogen atoms of the ligands are located at the corners of the triangles. The primed set of coordinates marks the projection of axes corresponding to an undistorted octahedron of ligand atoms.

hence may undergo a direct backward electron transfer reaction. The latter type of magnetic-field-induced reactivity of a radical pair is not known from normal radical pair theory. It is, however, a characteristic feature of the triplet mechanism where the magnetic field mixes triplet substates which are differently coupled to singlet reaction channels by SOC [13, 22].

2.3. Spin state transition induced by rotational motion of the Ru-complex

In order to account for anisotropic SOC in the Ru(III) complex moiety the spin states of the RP had to be described in a coordinate system fixed to the principal axes of the complex (cf. Fig. 1). We will now consider how the effective spin functions of the RP are transformed upon rotation of the complex. Rotation of the MV^+ radical does not change the representation of the effective RP spin functions because the orbital of the unpaired electron adiabatically follows the rotation of MO r , whereas its spin remains unchanged in a frame which is independent of the MV^+ orientation, since it is completely decoupled from orbital motion [23]. Rotating the Ru complex will have an effect on the representation of the effective spin function of the complex (X_{Ru}) and of the MV^+ radical (X_{MV}), which may be expressed as:

$$\mathbf{R}_{\varphi_u}(X_{\text{Ru}}' X_{\text{MV}}) = (\mathbf{R}_{\varphi_u} X_{\text{Ru}}')(\mathbf{R}_{\varphi_u} X_{\text{MV}}). \quad (15)$$

Here $\mathbf{R}_{\varphi_u}$ is a general rotation operator for a rotation of the Ru complex by an angle φ around an axis u . The effect of this rotation on the spin function X_{MV} results from the fact that the coordinate system, wherein

the spin function is described, is rotated. Such a transformation may be expressed by the following function of the spin operator $S_{MV,u}$ corresponding to the MV^+ spin component along the axis u of rotation of the coordinate system fixed in the Ru-complex:

$$R_{\varphi_u} X_{MV} = \exp(i\varphi_u S_{MV,u}) X_{MV}. \quad (16)$$

Application of Eq. (16) is straightforward since the spin functions α_{MV}, β_{MV} span a complete representation of the spinor group U_2 . The same is not true of the Kramers doublet $(\alpha'_{Ru}, \beta'_{Ru})$ because an arbitrary rotation of the *orbital* state will transform the *d*-orbitals among each other in such a way that the lowest Kramers doublet becomes mixed with higher electronic states. Such high-energy transitions are not expected to be feasible, however, at rotational velocities corresponding to thermal motion at room temperature. Instead, our assumption will be that the molecular rotation of the Ru(III) complex corresponds to an adiabatic perturbation in terms of time dependent perturbation theory [24]. Hence the transformation of the Kramers doublet $(\alpha'_{Ru}, \beta'_{Ru})$ on rotation of the complex will be treated in such a way that, during a differential rotation $d\varphi_u$, first the complete spin-orbit representation of the wavefunction (considered as fixed in the laboratory system) is transformed according to a rotation of the coordinate system and then it is projected onto the *rotated* basis set of the lowest Kramers doublet $(\alpha'_{Ru}, \beta'_{Ru})_{\varphi_u + d\varphi_u}$. The integrated result may be cast in the form

$$R_{\varphi_u} X'_{Ru} = \exp(i\varphi_u \gamma S_{Ru}^{\text{eff}}) X'_{Ru} \quad (17)$$

where φ_u is a vector of length φ_u directed along the axis of rotation u . The tensor γ is defined through the relation

$$\gamma S_{Ru}^{\text{eff}} \equiv P_{KD} (L_{Ru} + S_{Ru}) P_{KD} \quad (18)$$

where $L_{Ru} + S_{Ru}$ is the total electronic angular momentum operator and P_{KD} an operator projecting onto the linear space of the Kramers doublet. This definition is quite analogous to that of the *g*-tensor, in which case the operator $L_{Ru} + 2S_{Ru}$ has to be projected. The tensor γ is diagonal in the symmetry-adapted coordinate system of the complex with

$$\gamma_{\parallel} = \gamma_{zz} = \sin^2(x) - 3\cos^2(x) \quad (19a)$$

$$\gamma_{\perp} = \gamma_{xx} = \gamma_{yy} = 2\sqrt{2} \sin(x) \cos(x) + \sin^2(x). \quad (19b)$$

In deriving these expressions, *d*-orbital dilution by ligand orbitals has been neglected.

The rotation operator for each of the doublet species may be represented by means of the Pauli matrices in the respective doublet spin space:

$$R_{\varphi_u} = \cos\left(\frac{1}{2} A \varphi\right) \mathbf{I} + \frac{i}{A} \sin\left(\frac{1}{2} A \varphi\right) (u_x \gamma_{xx} \sigma_x + u_y \gamma_{yy} \sigma_y + u_z \gamma_{zz} \sigma_z) \quad (20)$$

where $\mathbf{I}$ denotes the unity matrix and

$$A = (u_x^2 \gamma_{xx}^2 + u_y^2 \gamma_{yy}^2 + u_z^2 \gamma_{zz}^2)^{1/2}. \quad (21)$$

The matrix representation of the rotation operator in the basis of product spin functions (7) is the direct product of the corresponding matrices $\mathbf{R}_{\varphi_u}(\gamma_{Ru(III)})$ and $\mathbf{R}_{\varphi_u}(\gamma_{Mv+})$, whereby $\gamma_{Mv+} = \mathbf{I}$. After transforming to the coupled basis (10), one obtains the following matrices for rotation about the main axis of the Ru complex.

$\mathbf{R}_{\varphi_x} =$

$$\begin{pmatrix} \cos\left(\frac{\gamma_{\perp}}{2}\varphi\right)\cos\left(\frac{\varphi}{2}\right) & -\sin\left(\frac{\gamma_{\perp}}{2}\varphi\right)\sin\left(\frac{\varphi}{2}\right) & \frac{i}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] - \frac{i}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] & \\ -\sin\left(\frac{\gamma_{\perp}}{2}\varphi\right)\sin\left(\frac{\varphi}{2}\right) & \cos\left(\frac{\gamma_{\perp}}{2}\varphi\right)\cos\left(\frac{\varphi}{2}\right) & \frac{i}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & \frac{i}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] \\ \frac{i}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & \frac{i}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & \cos\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & 0 \\ -\frac{i}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] & \frac{i}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] & 0 & \cos\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] \end{pmatrix} \quad (22a)$$

$\mathbf{R}_{\varphi_y}$

$$\begin{pmatrix} \cos\left(\frac{\gamma_{\perp}}{2}\varphi\right)\cos\left(\frac{\varphi}{2}\right) & \sin\left(\frac{\gamma_{\perp}}{2}\varphi\right)\sin\left(\frac{\varphi}{2}\right) & \frac{1}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & -\frac{1}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] \\ \sin\left(\frac{\gamma_{\perp}}{2}\varphi\right)\sin\left(\frac{\varphi}{2}\right) & \cos\left(\frac{\gamma_{\perp}}{2}\varphi\right)\cos\left(\frac{\varphi}{2}\right) & -\frac{1}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & -\frac{1}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] \\ -\frac{1}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & \frac{1}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & \cos\left[\frac{\varphi}{2}(\gamma_{\perp}+1)\right] & 0 \\ \frac{1}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] & \frac{1}{\sqrt{2}}\sin\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] & 0 & \cos\left[\frac{\varphi}{2}(\gamma_{\perp}-1)\right] \end{pmatrix} \quad (22b)$$

$$\mathbf{R}_{\varphi_z} = \begin{pmatrix} \exp\left[i\frac{\varphi}{2}(\gamma_{\parallel} + 1)\right] & 0 & 0 & 0 \\ 0 & \exp\left[-i\frac{\varphi}{2}(\gamma_{\parallel} + 1)\right] & 0 & 0 \\ 0 & 0 & \cos\left[\frac{\varphi}{2}(\gamma_{\parallel} - 1)\right] & i\sin\left[\frac{\varphi}{2}(\gamma_{\parallel} - 1)\right] \\ 0 & 0 & i\sin\left[\frac{\varphi}{2}(\gamma_{\parallel} - 1)\right] & \cos\left[\frac{\varphi}{2}(\gamma_{\parallel} - 1)\right] \end{pmatrix} \quad (22c)$$

As can be seen, rotating the Ru complex induces T'/S' mixing in the RP by virtue of SOC causing the components of $\gamma_{\text{Ru(III)}}$ to deviate from 1 (cf. Eqs. 19).

2.4. Dynamical treatment of redox pair decay

We describe the decay of the RP by two first order rate constants: k_{ce} , the rate constant of cage escape, and k_{bet} , a rate constant of spin-allowed backward electron transfer. Thereby it will be assumed that in the various RP spin substates i , the actual values of $k_{\text{bet},i}$ are given by

$$k_{\text{bet},i} = p_i^S k_{\text{bet}}, \quad (23)$$

whereby p_i^S is the true singlet character of substate i and can be obtained from the corresponding expansion coefficients in Eqs. (10).

Using the RP spin density matrix ϱ to describe the population and phase relations of the various spin states in an ensemble of RPs the equation of motion for a fixed orientation Ω of Ru complexes is:

$$\dot{\varrho} = -\frac{i}{\hbar}[\mathbf{H}_{\Omega}, \varrho] - \frac{1}{2}[\mathbf{K}_{\text{bet}}, \varrho]_+ - k_{\text{ce}}\varrho \quad (24)$$

with $[\]_-$ the commutator, $[\]_+$ the anticommutator and

$$\mathbf{K}_{\text{bet}} = k_{\text{bet}} \text{diag}(p_{T_+}^S, p_{T_-}^S, p_{T_0}^S, p_{S'}^S). \quad (25)$$

The stochastic Liouville Eq. (24) was integrated numerically, whereby the orientation Ω was subjected to a stochastic rotational diffusion process. The average $\bar{\varrho}(t)$ over a representative ensemble of diffusional trajectories was determined in a Monte Carlo type calculation.

The observable η_{ce} is obtained from $\bar{\rho}(t)$ by evaluating

$$\eta_{ce} = k_{ce} \int_0^{\infty} \text{Tr}[\bar{\rho}(t)] dt. \quad (26)$$

Since the Monte Carlo calculations were rather time consuming (about 8 h processor time on a Micro Vax 3600 for a typical calculation of one η_{ce} value at a fixed magnetic field), we developed an approximation where the explicit effect of rotational diffusion in a *dynamic* ensemble of RPs was approximated as an effective spin relaxation process in a *static* ensemble. The corresponding superoperator of spin relaxation was obtained as

$$\mathcal{R} = \left[\frac{d}{dt} \bar{\mathcal{R}}_x \right]_{t \rightarrow 0} + \left[\frac{d}{dt} \bar{\mathcal{R}}_y \right]_{t \rightarrow 0} + \left[\frac{d}{dt} \bar{\mathcal{R}}_z \right]_{t \rightarrow 0} \quad (27)$$

whereby $\bar{\mathcal{R}}_x(t)$, $\bar{\mathcal{R}}_y(t)$ and $\bar{\mathcal{R}}_z(t)$ are time dependent superoperators describing the evolution of the density matrix due to the rotational diffusion e.g.

$$\bar{\mathcal{R}}_x(t) = \int_{\varphi = -\infty}^{\infty} f(\varphi, t) \mathcal{R}_{\varphi_x} d\varphi \quad (28)$$

whereby

$$\mathcal{R}_{\varphi_x} \rho \equiv \mathbf{R}_{\varphi_x} \rho \mathbf{R}_{\varphi_x}^{-1} \quad (29)$$

and

$$f(\varphi, t) = (4\pi D_r t)^{-1/2} \exp[-\varphi^2/(4D_r t)] \quad (30)$$

is the angular distribution obtained after time t from a δ -type distribution as a result of rotational diffusion. The elements of the relaxation superoperator are given in the appendix.

This approach is based on the following arguments. Actually, applying the operator $\mathcal{R}$, defined in Eq. (27), to the density matrix of an ensemble of RPs with some fixed orientation, yields the time evolution of its density matrix (in the molecular frame) as the orientation of the ensemble spreads out by rotational diffusion. If the initial orientation distribution of RPs is isotropic, for every RP jumping into some new orientation, there will be one arriving at the considered initial orientational from a contiguous orientation by a rotational jump of the same width and in the same direction. Therefore, if the density matrix (in the molecular frame) is also independent of orientation, which holds exactly at zero field, the density matrix of RPs at the initial orientation changes in the same way as the density matrix of the RPs that were initially at this orientation. Under such conditions the operator defined in Eq. (27) is the exact local relaxation operator.

In a magnetic field the initial isotropic distribution of RP orientations is distorted and the density matrix becomes orientation dependent due to the anisotropy of magnetic interaction controlling the kinetic decay of RPs. Then a net flux of a rotational diffusion to the orientations with maximal magnetic field enhancement of RP decay contributes to the overall dynamics. In the quasi-static ensemble approximation, where exchange of population between different orientations is not explicitly taken into account, the effect of orientational flux is obviously well compensated by employing the orientational independent zero-field relaxation operator in the molecular frame. At present the justification of the quasi static ensemble model, which also has been successfully applied to the triplet mechanism [28], is mainly based on its excellent numerical agreement with the Monte Carlo results. Nevertheless a more rigorous formal justification would be desirable.

The stochastic Liouville equation to be solved for the equivalent static ensemble distributed over all orientations Ω is:

$$\dot{\mathbf{q}}_{\Omega} = -\frac{i}{\hbar}[\mathbf{H}_{\Omega}, \mathbf{q}_{\Omega}]_{-} + \mathcal{R}\mathbf{q}_{\Omega} - \frac{1}{2}[K_{\text{bet}}, \mathbf{q}_{\Omega}]_{+} - k_{\text{ce}}\mathbf{q}_{\Omega} \equiv \mathcal{L}_{\Omega}\mathbf{q}_{\Omega}. \quad (31)$$

It can be formally time-integrated and the result for $\tilde{\mathbf{q}}_{\Omega}$ is directly obtained as a solution of a system of 16 coupled linear equations.

$$\tilde{\mathbf{q}}_{\Omega} \equiv \int_{t=0}^{\infty} \mathbf{q}_{\Omega}(t) dt = -\mathcal{L}_{\Omega}^{-1} \mathbf{q}_{\Omega}(t=0). \quad (32)$$

Finally the isotropic angular average over Ω is performed. The results obtained in this way were practically identical to the results with the Monte Carlo technique. However, the computer time was reduced by more than 3 orders of magnitude.

3. Model calculations

By applying the dynamic theory described in the last section, one should be able to account for the observed net yield of cage escape [5] $\eta_{\text{net}} \approx 0.25$ with the $[\text{Ru}(\text{bpy})_3^{3+} \dots \text{MV}^+]$ RP and for the relative magnetic field dependence $R_{\eta_{\text{ce}}}(B_0)$ of this quantity as depicted in Figs. 3–5.

The following parameters have to be fixed in the model calculations: The g and γ -tensor of the RuL_3^{3+} complex, its rotational diffusion constant D_r , and the rate constants of cage escape k_{ce} and spin-allowed backward electron transfer k_{bet} .

In the calculations reported below, g and γ -tensor have been calculated from Eqs. (13) and (19), using a mixing angle of $\alpha = 67.5^\circ$ and neglecting orbital dilution of d -orbitals, i.e. setting $k = 1$ in Eqs. (13). This angle corresponds to the value obtained by DeSimone and Drago [25] from the

experimental g -tensor components $g_{\parallel}$ (1.14) and $g_{\perp}$ (2.64). (To obtain the experimental values exactly, k has to be given a value of 0.932. For $k = 1$ the corresponding g -tensor components are 1.12 and 2.71. This slight difference with respect to the experimental values has no significant effect on the results of the calculations.)

The standard value of D_r has been chosen as 1 ns^{-1} . According to the Debye equation,

$$D_r = \frac{k_B T}{8 \pi R^3 \eta}, \quad (33)$$

using a value of 1 cP for the solvent viscosity η , this corresponds to a hydrodynamic radius of $R = 5.5 \text{ \AA}$. (This value is somewhat smaller than the value of $7 \text{ \AA}$, usually assumed in the literature [5, 26] when estimating the translational diffusion coefficient. A value of $D_r = 0.5 \text{ ns}^{-1}$ would be consistent with such a radius. On the other hand, from experimental NMR relaxation studies [27], a value of $D_r = 1.7 \text{ ns}^{-1}$ can be derived.)

For k_{ce} , values may be estimated on the basis of the Eigen-Debye equation [5]. For low ionic strength a value of $k_{ce} = 5 \text{ ns}^{-1}$ is a reasonable order of magnitude.

With respect to the choice of k_{bet} it is of interest to note that from a kinetic estimate neglecting any differential reactivity of RP spin substates (cf. Eq. 1) an average value of $\bar{k}_{bet} = 8 \text{ ns}^{-1}$ has been obtained [5]. Of course, for a hypothetically spin-allowed process, the corresponding value should be significantly faster. Therefore, in the first trial calculations (cf. Fig. 2), we employed a value of $k_{bet} = 50 \text{ ns}^{-1}$.

In evaluating the theoretical model, the initial population of RP spin substates as originating in the photoinduced forward electron transfer step, is of great significance. One should assume that no spin change occurs during the fast forward electron transfer. The initial population of RP spin substates would then be obtained by performing a spin-conserving projection of the photoreactive (luminescent) MLCT state(s) of the RuL_3^{2+} complex onto the space of effective RP spin substates, whereby the π^* electron is transferred from a reduced Ligand L^- to the acceptor MV^{2+} . There has been a long debate in the literature on the appropriate representation of the (set of) luminescent RuL_3^{2+} state(s) [6–12]. We will not take up this problem here explicitly, but instead treat the initial population by an empirical parameter to be chosen in accord with the experimental results. Of course, the final choice will bear some implications on the electronic nature of the photoreactive state.

The results obtained by the density matrix formalism described in section 2 may be rationalized in terms of an approximately equivalent scheme depicted in Scheme II.

Spin relaxation and magnetic-field induced mixing cause equilibration between the formal spin substates of the RP, whereby equilibrium is ap-

Scheme II

Fig. 2. Calculated magnetic field dependence of η_{ce} for the cases where the RP originates in a single spin-substate. Parameter values were $D_r = 1 \text{ ns}^{-1}$, $k_{ce} = 5 \text{ ns}^{-1}$, $k_{bet} = 50 \text{ ns}^{-1}$. Experimental data points (from Ref. [4]) are indicated by +.

proached in two stages. The T' states equilibrate with an effective rate constant of

$$w_{TT} \approx a_{TT} D_r + b_{TT} B_0, \quad (34)$$

whereas relaxation between the equilibrated T' states and S' takes place at a rate of

$$w_{TS} \approx a_{TS} D_r + b_{TS} B_0. \quad (35)$$

With the g and γ -tensor component values chosen above, the coefficients have the approximate values $a_{TT} \approx 10$, $a_{TS} \approx 1$, $b_{TT} \approx 100 \text{ ns}^{-1} \text{ T}^{-1}$ and $b_{TS} \approx 20 \text{ ns}^{-1} \text{ T}^{-1}$. Both coefficients are larger by approximately one order of magnitude in w_{TT} than in w_{TS} , which is a prerequisite of the conceptual separation of two time scales.

Fig. 3. Calculated relative MFE, $R_{\eta_{ce}}$, for various cases of initial S' -substate population. Corresponding values of parameter s are indicated in the figure. Parameter values $D_r = 1 \text{ ns}^{-1}$, $k_{ce} = 5 \text{ ns}^{-1}$ were kept constant; k_{bet} was adjusted so that $\eta_{ce}(B_0 = 0) = 0.25$. The following values of k_{bet} (in the order of increasing s) had to be employed: 528, 300, 200, 100, 50, 30, 20 ns^{-1} . Experimental data points are indicated by +.

The rate constant of cage escape (k_{ce}) is the same for all spin substates. the rate constant of backward electron transfer is much faster for S' than for $T'_\pm$ ($p_{S'}^S : p_{T'_\pm}^S \approx 10:1$), for T'_0 it is zero.

In Fig. 2 the results on the magnetic field dependence of η_{ce} are shown, obtained with the standard parameter set for the various cases where the RP is generated only in one of the substates S' , T'_0 or $T'_\pm$. For T' generation η_{ce} is much higher than the experimental value, for S' generation it is significantly lower. The magnetic field dependences exhibit different characteristics. For a RP created in T'_0 the magnetic field dependence reaches its steepest slope at a relatively low field of about 0.1 T. This effect is due to the large b_{TT} mixing term and brings η_{ce} for this case close to the zero-field starting point of the $T'_\pm$ case. Here η_{ce} is largely determined by the direct reaction possibility ($p_{T'_\pm}^S k_{bet}$) of $T'_\pm$. At fields higher than about 0.3 T, T'_0 and $T'_\pm$ are approximately in equilibrium during the RP decay, so that they show a similar magnetic field dependent decrease of η_{ce} at higher fields. This magnetic field dependence is due to the increase of $T' - S'$ mixing by virtue of the term $b_{TS}B_0$ in Eq. (35). Since b_{TS} is about 5 times smaller than b_{TT} , correspondingly higher fields are necessary to make this magnetic field effect contribution observable. At low fields, $T'_0 - T'_\pm$ equilibration responsible for the relatively steep initial magnetic field dependence of η_{ce} , when the RP is generated in T'_0 , has just the opposite effect when starting in $T'_\pm$.

Fig. 4. Calculated relative MFE, $R_{\eta_{ce}}$, for initial T' -substate population only (i.e. $s = 0$). Other parameter values are $k_{ce} = 5 \text{ ns}^{-1}$; D_r is varied as indicated in the figure (values in ns^{-1}); k_{bet} was adjusted so that $\eta_{ce}(B_0 = 0) = 0.25$. The following values of k_{bet} (in the order of increasing D_r) had to be employed: 528, 394, 352, 269, 213, 174 ns^{-1} . Experimental data points are indicated by +.

In this case η_{ce} exhibits a slight increase at low fields because the equilibrated T' mixture recombines less efficiently than $T'_\pm$.

If the RP is created in S' , a positive MFE on η_{ce} is obtained. The onset of the effect that is based on the b_{TS} -dependent $S' - T'$ mixing coincides with the field region where the T'_0 and $T'_\pm$ curves start to run parallel. The reason for the magnetic field dependent increase of η_{ce} is obvious: the equilibrated S'/T' mixture has a smaller average recombination constant than a mixture more enriched in S' .

In the next step of the fitting procedure, the theoretical parameter values to reproduce the experimental results on $\eta_{ce}(B_0)$ the initial populations P_i of the substates i were varied in terms of one parameter s [$P_{S'} = s$, $P_{T'_0} = P_{T'_+} = P_{T'_-} = (1-s)/3$]. At the same time the parameter k_{bet} was adjusted in such a way that $\eta_{ce}(B_0 = 0)$ fitted the experimental value of 0.25. The resultant curves for the relative MFE on η_{ce} :

$$R_{\eta_{ce}}(B_0) = \frac{\eta_{ce}(B_0) - \eta_{ce}(0)}{\eta_{ce}(0)} \quad (36)$$

are plotted in Fig. 3 for the full range of $0 \leq s \leq 1$. In order to obtain a negative MFE, s must be lower than 0.7. The correct order of magnitude of the MFE at high fields is obtained with $s \approx 0.59$ and $k_{bet} \approx 100 \text{ ns}^{-1}$. However, the general magnetic fields dependence is reproduced very poorly.

Fig. 5. Calculated relative MFE, $R_{\eta_{ce}}$, for an initial 45% ($s = 0.45$) S' population of the RP. Other parameter values are $k_{ce} = 5 \text{ ns}^{-1}$; D_r is varied as indicated in the figure (values in ns^{-1}); k_{bet} was adjusted so that $\eta_{ce}(B_0 = 0) = 0.25$. The following values of k_{bet} (in the order of increasing D_r) had to be employed: 165, 143, 120, 113, 107, 102 ns^{-1} . Experimental data points are indicated by +.

The onset of the magnetic field dependence is much steeper and the saturation is approached earlier than in the experiment. Within the present model of the mechanism this inadequacy of the fit can only be removed by allowing D_r to increase, i.e. to make relaxation among the formal RP spin-substates faster.

Fig. 4 shows a series of $R_{\eta_{ce}}(B_0)$ curves applying to the case of initial T' population only ($s = 0$) with D_r varied as indicated and k_{bet} determined by the condition $\eta_{ce}(0) = 0.25$. As one can see, the experimental curve does not fit well into this family of theoretical curves. If the fit is suitable at low fields (e.g. $D_r = 15 \text{ ns}^{-1}$, $k_{bet} = 238 \text{ ns}^{-1}$) the effect at high fields is predicted too high. This behaviour can be improved and even inverted (good fit at low fields, too small effect predicted at high fields) if the parameter s of initial S' population is allowed to increase. An optimum is achieved with $s = 0.45$, $D_r = 12.5 \text{ ns}^{-1}$ and $k_{bet} = 107 \text{ ns}^{-1}$ (cf. Fig. 5).

In Fig. 6 we present the explicit time dependence of the decay of the RP obtained with the parameter set of the optimum fit of $R_{\eta_{ce}}(B_0)$ in Fig. 5. The decay is not monoexponential. In the beginning the slope of the log-plot approximately corresponds to $s k_{bet} + k_{ce}$ and reflects the fast recombination of most of the initial S' population. Because, initially, the S' population exceeds its equilibrium value there is some net transfer of S' population to the T' manifold caused by spin relaxation and magnetic field induced mixing. This process is faster in a magnetic field and therefore

Fig. 6. Decay profiles of RP population calculated with parameters $k_{ce} = 5 \text{ ns}^{-1}$, $k_{bet} = 107 \text{ ns}^{-1}$, $D_r = 12.5 \text{ ns}^{-1}$, $s = 0.45$, corresponding to the best fit case in Fig. 5. The curves pertain to magnetic fields of 0, 1, 2, 3 T. The insert shows part of the decay with a log scale ordinate.

leads to a slightly reduced decay rate noticeable around 20 ps. As a more detailed analysis shows, a quasi stationary population ratio of T' to S' is achieved at about 30 ps. After that time, the decay is practically monoexponential with its rate constant, reflecting the quasi stationary value of the fraction of RPs present in S' , increasing with the magnetic field. The long term rate constant is the sum of k_{ce} and a magnetic field dependent overall rate constant $k_{bet}^{eff}(B_0)$. Values of the latter are 8 ns^{-1} (0 T), 11.6 ns^{-1} (1 T), 13.6 ns^{-1} (2 T), 14.8 ns^{-1} (3 T) showing a much more pronounced magnetic field dependence than η_{ce} . The reason for this difference lies in the fact that the strongly magnetic field dependent part of the decay commences only after almost 60% of the RPs have already decayed. This is a consequence of the high initial S' population that had to be assumed in order to model the experimental $\eta_{ce}(B_0)$ dependence.

4. Discussion

In the last section it has been shown that, formally, the observed MFE can be quantitatively accounted for within the limits of the theoretical framework set up in section 2. Now it will be in order to discuss the physical

implications of the values assigned to the parameters D_r , k_{bet} , s by virtue of the fitting procedure.

Actually, their determination is based on the choice of k_{ce} , relying on the validity of the Eigen-Debye equation, and of the spin-orbit mixing angle x , determined by DeSimone and Drago [25] from the experimental values of $|g_{\parallel}|$ and $|g_{\perp}|$ of $\text{Ru}(\text{bpy})_3^{3+}$. According to Eq. (13) the signs of both $g_{\parallel}$ and $g_{\perp}$ are positive when using their value of $x = 67.5^\circ$. It should be mentioned that an alternative value of $x = 45^\circ$ has been advocated by Kober and Meyer [17]. With this angle the sign of $g_{\parallel}$ becomes negative and the $T'_0 - S'$ coupling by the Zeeman Hamiltonian (Eq. 14) increases considerably. As it turned out, a satisfactory fit of the experimental MFE was not possible with the latter choice of x .

The value of $s = 0.45$ required in the final set of fitting parameters signifies a surprisingly high initial singlet population of the RP. It is difficult, at present, to reconcile it with the widely accepted notion of the reacting MLCT of $\text{Ru}(\text{bpy})_3^{2+}$ as being of predominant triplet character. A more detailed analysis of the various electronic models suggested in the literature [6, 9, 10] for the lowest excited spin-orbit states of the complex may provide a basis to understand this feature.

The value of $k_{\text{bet}} = 107 \text{ ns}^{-1} \approx 10^{11} \text{ s}^{-1}$ evaluated for the rate constant of spin-allowed backward electron transfer corresponds to an order of magnitude characteristic for diabatic activationless electron transfer processes, a situation to be expected if ΔG_{bet} corresponds to the vertex position of the Marcus parabola. To observe the calculated decay curve of the RP (Fig. 6), it would be interesting to do a ps time-resolved experiment. This should be performed with a supermolecular aggregate of Ru-complex and electron acceptor, however, in order to eliminate the diffusion controlled formation of an encounter complex as a rate determining step in the creation of the $[\text{Ru}(\text{bpy})_3^{3+} \dots \text{MV}^+]$ RP.

The final value fixed for D_r (12.5 ns^{-1}) turns out to be much faster than reasonably expected for rotational diffusion ($\approx 1 \text{ ns}^{-1}$) of the $\text{Ru}(\text{bpy})_3^{3+}$ complex. In order to account for this finding one has to resort to a reinterpretation of the source of spin relaxation. In setting up the superoperator $\mathcal{R}$ it has been assumed that rotational diffusion of the Ru complex provides the essential relaxation mechanism. One could, however, conceive the form of $\mathcal{R}$ derived in section 2 as a parameterized form of a general relaxation operator, with $1/D_r$ representing some characteristic correlation time and the γ -tensor accounting for the strength of some fluctuating perturbation responsible for the relaxation. Obviously, then, the numerical result for D_r points to a relaxation mechanism different from and much more effective than rotational diffusion. Possibly it is related to vibrational motion of the ligands around their equilibrium positions in the coordination sphere of the Ru ion. Of course, the functional form of the matrix elements would have to be modified in compliance with the correct relaxation mechanism,

in order to make the reinterpretation of the fit consistent with the modified model.

As a final comment in this discussion, we would like to mention the possible effect of electron exchange interaction in the RP $[\text{Ru}(\text{bpy})_3^{3+} \dots \text{MV}^+]$. Such an interaction, that we are about to study in a parametrized form, will cause a splitting of the RP levels T'_0 , $T'_\pm$ and S' according to their respective singlet character. This zero-field splitting of RP spin substates will impede the level mixing by a magnetic field and will give rise to level anticrossing phenomena in certain field regions. It is possible that a realistic account of such effects could explain the slow saturation behaviour characterizing the experimentally observed MFE, so that no extraordinarily high values of D_r would have to be adopted.

5. Conclusions

In this work we have described the theoretical principles for dealing in a formally consistent way with the magnetokinetic behaviour of a redox pair comprising a strongly spin-orbit mixed Kramers doublet species $[\text{Ru}(\text{bpy})_3^{3+}]$ and a normal π -radical (MV^+). From the point of view of magnetokinetic mechanisms, the present case combines features of both the Δg -type radical pair mechanism and the triplet mechanism.

An efficient numerical procedure has been developed allowing for a quantitative comparison of the mechanistic model with the experimentally determined magnetic field dependence of the efficiency of cage escape (η_{ce}). Fitting the experimental results allows us to determine a unique set of model parameters including the value of the rate constant of spin-allowed backward electron transfer (k_{bet}).

As shown in the discussion, a physically consistent interpretation of the magnetic field effect requires and may help to achieve an advanced understanding of several elementary processes and problems associated with the backward electron transfer process. These problems concern the mechanism of spin relaxation, the spin situation in the photoreactive state of the Ru-complex and the role of exchange interaction in the $[\text{Ru}(\text{bpy})_3^{3+} \dots \text{MV}^+]$ redox pair.

Acknowledgement

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Appendix

Relaxation superoperator

Non-zero elements of the symmetric relaxation superoperator matrix ($\mathcal{R}_{ij,kl}$ denoting supermatrix elements with reference to the basis T'_+ , T'_- , T'_0 , S'

of the density matrix) are given in the following shorthand notation. The γ -dependent terms on the left are positive or negative (if $\mathcal{R}_{ij,kl}$ appears with a minus sign) contributions to the matrix elements of $\mathcal{R}$ listed on the right.

$$\begin{aligned}
 -(\gamma_{\perp}^2 + 1) D_r: & \quad \mathcal{R}_{11,11}, \mathcal{R}_{12,12}, \mathcal{R}_{21,21}, \mathcal{R}_{22,22}, \mathcal{R}_{34,34}, \mathcal{R}_{43,43} \\
 \frac{1}{2}(\gamma_{\perp} + 1)^2 D_r: & \quad \mathcal{R}_{11,33}, \mathcal{R}_{13,32}, \mathcal{R}_{22,33}, \mathcal{R}_{23,31} \\
 \frac{1}{2}(\gamma_{\perp} - 1)^2 D_r: & \quad \mathcal{R}_{11,44}, -\mathcal{R}_{14,42}, \mathcal{R}_{22,44}, -\mathcal{R}_{24,41} \\
 -(\gamma_{\perp} + 1)^2 D_r: & \quad \mathcal{R}_{33,33} \\
 -(\gamma_{\perp} - 1)^2 D_r: & \quad \mathcal{R}_{44,44} \\
 \frac{1}{2}(\gamma_{\perp}^2 - 1) D_r: & \quad -\mathcal{R}_{11,34}, -\mathcal{R}_{11,43}, -\mathcal{R}_{13,42}, \mathcal{R}_{14,32}, \mathcal{R}_{22,34}, \\
 & \quad \mathcal{R}_{22,43}, \mathcal{R}_{23,41}, -\mathcal{R}_{24,31} \\
 -(\gamma_{\parallel} + 1)^2 D_r: & \quad \mathcal{R}_{12,12}, \mathcal{R}_{21,21} \\
 -\frac{1}{2}(\gamma_{\parallel}^2 + 1) D_r: & \quad \mathcal{R}_{13,13}, \mathcal{R}_{14,14}, \mathcal{R}_{23,23}, \mathcal{R}_{24,24}, \mathcal{R}_{31,31}, \mathcal{R}_{32,32}, \\
 & \quad \mathcal{R}_{41,41}, \mathcal{R}_{42,42} \\
 \frac{1}{2}(\gamma_{\parallel}^2 - 1) D_r: & \quad \mathcal{R}_{13,14}, -\mathcal{R}_{23,24}, \mathcal{R}_{31,41}, -\mathcal{R}_{32,42} \\
 \frac{1}{2}(\gamma_{\parallel} - 1)^2 D_r: & \quad -\mathcal{R}_{33,33}, \mathcal{R}_{33,44}, -\mathcal{R}_{34,34}, \mathcal{R}_{34,43}, -\mathcal{R}_{43,43}, \\
 & \quad -\mathcal{R}_{44,44} \\
 -(\gamma_{\perp}^2 + \gamma_{\perp} + 1) D_r: & \quad \mathcal{R}_{13,13}, \mathcal{R}_{23,23}, \mathcal{R}_{31,31}, \mathcal{R}_{32,32} \\
 -(\gamma_{\perp}^2 - \gamma_{\perp} + 1) D_r: & \quad \mathcal{R}_{14,14}, \mathcal{R}_{24,24}, \mathcal{R}_{41,41}, \mathcal{R}_{42,42}
 \end{aligned}$$

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