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Internal conversion induced by external electric and magnetic fields†

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We have developed a new methodology for calculating contributions to the rate constants (k_{IC}) of internal conversion that are induced by external electric ($k_{IC\text{-}E}$) or magnetic ($k_{IC\text{-}M}$) fields. The influence of the external electric and magnetic fields on the k_{IC} was estimated for seven representative molecules. We show that the $k_{IC\text{-}E}$ contribution calculated at a field strength of 10^{11} V m^{-1} is generally as large as the k_{IC} rate constant in the absence of the external field. For indocyanine green, azaoxa[8]circulene, and pyromitene 567, the $k_{IC\text{-}E}$ contribution is as large as k_{IC} already at a field strength of 10^9 V m^{-1}. Such electric-field strengths occur for example in plasmonic studies and in strong laser-field experiments. The induced effect on the k_{IC} rate constant should be accounted for in calculations of photophysical properties of molecules involved in such experiments. The induced effect of an external magnetic field on k_{IC} can be neglected in experiments on Earth because the magnetic contribution becomes significant only at very strong magnetic fields of 10^4–10^5 T that cannot be achieved on Earth. However, the magnetic effect on the rate constant of internal conversion can be important in astrophysical studies, where extremely strong magnetic fields occur near neutron stars and white dwarfs.

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1. Introduction

The interaction of electromagnetic fields with matter at the molecular level is one of the main tasks in photophysical studies[1–7] since the knowledge of the energies of electronic states and their lifetime are important for understanding molecular luminescence properties.[8–10] The energy of excited states can at low molecular concentration be converted to vibrational energy of lower-lying states by nonradiative transitions and to light by radiative intramolecular electronic transitions.[11] The intramolecular nonradiative electronic transitions are the internal conversion (IC) and the intersystem crossing (ISC). The IC process is the electronic transition between states with the same electron spin and the ISC transition occurs between states with different spin. The radiative transition between the singlet electronic states is called fluorescence and phosphorescence between state with different spin multiplicity.

The expressions for the rate constants can be derived by using first-order perturbation theory.[12] The nonadiabatic coupling interaction (NAC) operator is the perturbation operator in case of IC and the spin–orbit coupling (SOC) interaction operator is the perturbation operator of the ISC process. The electric dipole operator is the perturbation operator for fluorescence when adopting the electric dipole approximation. A variety of theoretical models for quantum chemical calculations of rate constants or deactivation-channel probabilities of electronic excited states of isolated molecules have been developed by many research groups.[12–19] More deactivation channels are opened when the molecule interacts with an electromagnetic field. For example, when a molecule is located near a plasmonic nanoparticle, the radiative rate constant or fluorescence efficiency can be strongly enhanced or it decreases due to the interaction with the electromagnetic field of the plasmon,[7] which also influences the fluorescence quantum yield. In general, it is assumed that the rate constants of IC and ISC are not significantly affected when a molecule is in the vicinity of a plasmonic system or by a strong laser field.[20–22] However, this assumption can be questioned. Strek estimated the influence of external electric fields on the internal conversion rate constant (k_{IC}) using a simple model.[23] It was shown that an external electric field of 10^8–10^9 V m^{-1} can strongly influence the k_{IC} rate constant. An electric field of that strength is comparable to the strength of the plasmonic field of nanoparticles.[7]

In this work, we derive expressions for calculating rate constants of internal conversion for molecules that are exposed to strong electric or magnetic fields. The expressions have been adapted for quantum chemical calculations. We use the new theoretical model in calculation of rate constants of internal conversion to estimate the influence of external electric and magnetic fields on the k_{IC} rate constants. The methods are applied to molecules that emit light in the infrared, red, green, blue, and ultraviolet range of the spectrum. The studied

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molecules are isophlorin (**ISO**), indocyanine green (**ICG**), pyromitene (**PM567**) azaoxa[8]circulene (**4B**), 2,2″-dimethyl-*p*-terphenyl (**BM-Terphenyl**), 2-(4-Biphenylyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazol (**BPBD-365**) and 2-(1-Naphthyl)-5-phenyloxazol (**a-NPO**).

2. Theory and computations

2.1. Internal conversion in the absence of external fields

In the works of Plotnikov[24] and Artyukhov[25] as well as in our recent studies,[12,15] it was shown that the approximation, where the energy of the first excited singlet state (S_1) is converted mainly into the vibrations of the X–H bonds (X = N, O and C), yields k_{IC} values that agree within one order of magnitude with those calculated at more accurate levels of theory. The k_{IC} rate constant between the p and q states is then given by

$$k_{IC}(p \to q) = \frac{\left\langle \psi_p \middle| \hat{\Lambda} \middle| \psi_q \right\rangle^2}{E_{pq}^2} \cdot Q_{pq}, \tag{1}$$

where Ψ_p is the wave function of the initial electronic state, Ψ_p is the wave function of the final electronic state, $\langle \psi_p | \hat{\Lambda} | \psi_q \rangle$ with $\hat{\Lambda} = \sum_{\alpha=1}^{N_{XH}} \frac{\partial U}{\partial R_\alpha}$ is the matrix element of the nonadiabatic coupling operator (NACME) between Ψ_p and Ψ_p, and E_{pq} is energy difference between the p and q states. The R_α coordinate is along the α-th X–H bond. Q_{pq} is a vibrational factor that can be written as

$$Q_{pq} = N_{XH} \times 6.25 \times 10^6 \times e^{-E_{pq}/2.17} \tag{2}$$

Here, N_{XH} is the number of accepting X–H modes, E_{pq} in the expressions (1) and (2) is the energy difference in 10^3 cm^{-1}. The expression for the square of the NACME can be written as

$$\left\langle \psi_p \middle| \hat{\Lambda} \middle| \psi_q \right\rangle^2 = \sum_{\alpha=1}^{N_{XH}} \left| \sum_{ia} \sum_{jb} A_{ia}^p A_{jb}^q \langle i \to a | \frac{\partial U}{\partial R_\alpha} | j \to b \rangle \right|_\alpha^2, \tag{3}$$

where $|i \to a\rangle$ and $|j \to b\rangle$ are Slater determinants and $A_{ia}{}^p$, $A_{jb}{}^q$ are configurational interaction coefficients. The a, b are indices denote virtual molecular orbitals (MO) and i, j are indices of the occupied MOs. The NACME in (3) is non-zero when the left and right determinants differ by at most one MO because $\hat{\Lambda}$ is one electron operator. Expression (3) consists of two terms:

$$\left\langle \psi_p \middle| \hat{\Lambda} \middle| \psi_q \right\rangle^2 = \sum_{\alpha=1}^{N_{XH}} \left| \sum_{ia} \sum_{b} A_{ia}^p A_{ib}^q \langle a | \frac{\partial U}{\partial R_\alpha} | b \rangle + \sum_{ia} \sum_{ja} A_{ia}^p A_{ja}^q \langle i | \frac{\partial U}{\partial R_\alpha} | j \rangle \right|_\alpha^2 \tag{4}$$

The MOs are expanded in the basis functions (χ) located at the X–H bonds yielding the final expression for NACME:

$$\left\langle \psi_p \middle| \hat{\Lambda} \middle| \psi_q \right\rangle^2 = \sum_{\alpha=1}^{N_{XH}} \left| \sum_{iabkk'} A_{ia}^p A_{ib}^q c_a^k c_b^{k'} \left\langle \chi_a^k \middle| \frac{\partial U}{\partial R_\alpha} \middle| \chi_b^{k'} \right\rangle + \sum_{ijakk'} A_{ia}^p A_{ja}^q c_i^k c_j^{k'} \left\langle \chi_i^k \middle| \frac{\partial U}{\partial R_\alpha} \middle| \chi_j^{k'} \right\rangle \right|_\alpha^2, \tag{5}$$

where $c_i{}^k$, $c_j{}^{k'}$, $c_a{}^k$, $c_b{}^{k'}$, are the MO coefficients. We assume that $\left\langle \chi_\alpha^k \middle| \frac{\partial U}{\partial R_\alpha} \middle| \chi_\alpha^k \right\rangle$ is 0.1 for each X–H bond. More details can be found in ref. 15 and 25. The final expression for k_{IC} can then be written as

$$k_{IC} = 1.6 \times 10^9 \cdot \langle \psi_p | \hat{\Lambda} | \psi_q \rangle^2, \tag{6}$$

where

$$\left\langle \psi_p \middle| \hat{\Lambda} \middle| \psi_q \right\rangle^2 = \left[\sum_{\alpha=1}^{N_{XH}} P_\alpha^2 \right] \cdot \frac{N_{XH} \cdot 6.25 \times 10^6 \cdot e^{-E_{pq}/2.17}}{E_{pq}^2} \tag{7}$$

where is the electronic factor $P_\alpha^2 = 0.01 \left| \sum_{iabkk'} A_{ia}^p A_{ib}^q c_a^k c_b^{k'} + \sum_{ijakk'} A_{ia}^p A_{ja}^q c_i^k c_j^{k'} \right|_\alpha^2$ for each X–H bond. Using this model, it is possible to estimate the individual contributions from each X–H mode to the NACME.

2.2. Internal conversion in the presence of electric or magnetic fields

The influence of external field on k_{IC} can be obtained by using second-order perturbation theory,[26] where $\hat{O} = \hat{\Lambda} + \vec{p} \cdot \vec{W}$ is the perturbation operator. $\vec{p}$ denotes the electric or the magnetic dipole-moment operator and $\vec{W}$ is the field strength. The zero order Hamiltonian is then

$$\hat{H}_0 = \sum_\alpha E_\alpha^0 a_\alpha^\dagger \hat{a}_\alpha + \sum_{\alpha,j} \hbar w_\alpha^j \hat{a}_\alpha^\dagger \hat{a}_\alpha \hat{b}_j^\dagger \hat{b}_j + \sum_{\alpha,j} g_\alpha^j \hbar w_\alpha^j \hat{a}_\alpha^\dagger \hat{a}_\alpha \left(\hat{b}_j^\dagger + \hat{b}_j \right). \tag{8}$$

Here $\hat{a}_\alpha$, $\hat{a}_\alpha^\dagger$ are fermion annihilation and creation operators of the electronic state α and $E_\alpha{}^0$ is its electronic energy. $\hat{b}_j$ and $\hat{b}_j^\dagger$ are the boson annihilation and creation operators of the phonons, $w_\alpha{}^j$ is the frequency of the j-th phonon, and $g_\alpha{}^j = (M_j w_j{}^\alpha / 2\hbar)^{1/2} \Delta R_j{}^\alpha$ is dimensionless parameter where $\Delta R_j{}^\alpha$ corresponds to the displacement from the equilibrium position of the ground state. $\hat{\Lambda}$ is the perturbation operator that in the absence of external fields gives the first-order contribution to the IC rate constant (k_{IC}). In the presence of external fields, the perturbation operator can either be $\hat{O} = \hat{\Lambda} + \vec{p}.\vec{W}$ or $\hat{O} = \vec{p} \cdot \vec{W}$. In the first case, the non-vanishing contribution to induced radiationless transition appears only at the second order of perturbation theory. When $\hat{O} = \vec{p} \cdot \vec{W}$, the radiative process is the first order and the induced radiationless transition appear at the second order without the $\hat{\Lambda}$ operator. Such process must occur in two steps[27,28] and has smaller contribution to the induced IC than with $\hat{O} = \hat{\Lambda} + \vec{p}.\vec{W}$. Therefore, we consider only the case with $\hat{O} = \hat{\Lambda} + \vec{p}.\vec{W}$ as the perturbation operator.

The electronic matrix elements of $\hat{O} = \hat{\Lambda} + \vec{p}.\vec{W}$ at the second-order perturbation theory level is

$$\langle p | \hat{O} | q \rangle = \sum_{s \neq p,q} \sum_j \left[P_{qs}^j \langle s | \vec{p} | p \rangle + \langle q | \vec{p} | s \rangle P_{sp}^j \right] \cdot \left[\frac{1}{E_p - E_s} \right] W \tag{9}$$

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Here, $P_{sp}{}^{j}$ is electronic factor of the j-th mode between the electronic p and s states. The q and p can be associated with the singlet electronic ground state (S_0) and the first excited electronic singlet state (S_1), respectively. The intermediate state s is an electronic state that is energetically above S_1. Eqn (7) can be simplified to

$$\langle S_1|\hat{O}|S_0\rangle = \sum_{\alpha} \tilde{P}_j W, \tag{10}$$

where

$$\tilde{P}_j = \sum_{s} \left[\frac{P^j_{qs}\langle s|\vec{p}|q\rangle + P^j_{sp}\langle p|\vec{p}|s\rangle}{E_p - E_s} \right] \tag{11}$$

Thus, external fields influence only the electronic factor. Eqn (11) can be inserted into eqn (7) yielding expression (10), which can be used for estimating the rate constants for internal conversion $k_{\text{IC-E}}$ and $k_{\text{IC-M}}$ in the presence of external electric or magnetic fields, respectively.

$$k_{\text{IC-P}} = \left(\sum_{j} \tilde{P}_j \right)^2 \frac{N_{\text{XH}} \cdot 6.25 \times 10^6 \cdot \mathrm{e}^{-E_{\text{pq}}/2.17}}{E^2_{\text{pq}}} W^2 \tag{12}$$

$\vec{p}$ is the electric dipole operator ($\vec{d}$) in case of an electric field and the magnetic dipole operator ($\vec{m}$) when the molecule is exposed to a magnetic field. Expression (10) shows that it is possible to estimate the influence of external fields separately for each vibrational mode *via* $\tilde{P}_j$.

The electric and magnetic transition moments between the electronic states q and s are given by $\langle q|\vec{d}|s\rangle$ and $\langle q|\frac{mB}{\hbar}\hat{L}|s\rangle$, respectively.

The X–H bond approximation of k_{IC} calculations can be used only for molecules having X–H bonds including organometallic compounds.[16,29,30]

2.3. Computational details

The molecular structure optimizations, calculations of the second derivative of the potential energy surface (hessian) of the S1 state and the electric (d_{if}) and magnetic (m_{if}) transition dipole moment between the S_i and S_f states were performed at the density functional theory (DFT) and the time-dependent density functional theory (TDDFT)[31,32] levels using the B3LYP[33] functional and the 6-31G**[34] basis set with the DALTON software.[35] We calculated P_j for the 50 lowest electronic states. We assume that the molecule is oriented such that the scalar product of E or B with the electric dipole moment or magnetic dipole moment is largest, which can is obtained when these vectors are collinear. $k_{\text{IC-E}}$ and $k_{\text{IC-M}}$ denote the contributions to the rate constants of internal conversion that are induced by electric or magnetic external fields, respectively.

To verify the role of double excitations, which are not explicitly considered at the TDDFT level, we calculated the 50 lowest electronic singlet states at the complete active space self-consistent (CASSCF) level for molecules with the smallest (**ISO**), medium (**4B**) and largest (**BM-Terphenyl**) excitation energy (S_1–S_0).[36] The active space consisted of 12 electrons in 12 molecular orbitals. The calculations were performed using Firefly.[37,38] The calculations show that the double excitations contribute with about less than 10% to the wavefunctions of the 50 excited states suggesting that the results obtained at the TDDFT level are reliable.

3. Result and discussion

Rate constants for internal conversion have been calculated for isophlorin (**ISO**), indocyanine green (**ICG**), pyromitene (**PM567**) azaoxa[8]circulene (**4B**), 2,2″-Dimethyl-*p*-terphenyl (**BM-Terphenyl**), 2-(4-Biphenylyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazol (**BPBD-365**) and 2-(1-Naphthyl)-5-phenyloxazol (**a-NPO**) at the B3LYP/6-31G** level using the approach described in Section 2. The calculated k_{IC} in the absence of external fields and the strengths of the electric (E) and magnetic (H) fields when induced contributions $k_{\text{IC-E}}$ and $k_{\text{IC-M}}$ are as large as k_{IC} are given in Table 1.

The electric-field induced contribution to $k_{\text{IC-E}}$ become as large as k_{IC} when the external electric field strength is stronger than 1.0×10^9–2.1×10^{11} V m^{-1}. An electric field of 10^{10}–10^{11} V m^{-1} is very strong and can be compared to the strength of the internal electric field in molecules caused by its electrons. When molecules are exposed to that strong external electric fields they might dissociate. However, a field strength of 1.0×10^9 V m^{-1} can be observed in molecules exhibiting plasmonic effects. Indocyanine molecules are widely used in plasmonic enhancement fluorescence measurements.[7] The dependence of $k_{\text{IC-E}}$ on E is a quadratic. At an electric field strength of 1.0×10^9 V m^{-1}, the $k_{\text{IC-E}}$ contribution to k_{IC} of **ICG** becomes one order of magnitude larger than the k_{IC} rate constant in the absence of the electric field. Thus, at the contribution to k_{IC} due to the electric field can significantly change its molecular photophysical properties implying that the $k_{\text{IC-E}}$ contribution must be considered when calculating the fluorescence quantum yield.[7] In general, the $k_{\text{IC-E}}$ contribution is larger than k_{IC} at a field strength of 10^{11} V m^{-1} and $k_{\text{IC-E}}$ does not significantly depend on the energy gap between S_1 and S_0.

The magnetic-field induced effect on IC is almost negligible at the experimental conditions on Earth because it becomes significant at very strong magnetic fields (B) of about 10^4 T. The $k_{\text{IC-M}}$ contribution does not depend on the energy gap between S_1 and S_0. The magnetic-field induced contribution to k_{IC} for

Table 1 The calculated energy gap (E_{pq} in cm^{-1}) between the initial (p) and final (q) states calculated at the B3LYP/6-31G** level as well as the calculated rate constants of internal conversion (in s^{-1}) between p and q. The strength of the electric field (E) is given in V m^{-1} and the strength of the magnetic field (B) is given in T

	E_{pq}	k_{IC}	E	B
ISO	7829	3.7×10^{10}	2.1×10^{11}	5.0×10^5
ICG	15 700	4.1×10^8	1.0×10^9	1.4×10^4
PM567	18 333	2.0×10^6	7.0×10^9	1.9×10^4
4B	21 637	6.6×10^6	5.7×10^9	1.4×10^4
a-NPO	24 180	3.2×10^6	9.0×10^{10}	1.7×10^4
BPBD-365	25 664	2.1×10^6	7.0×10^9	1.8×10^5
BM-Terphenyl	29 504	3.4×10^5	3.0×10^{10}	6.0×10^4

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isophlorin becomes as large as k_{IC} for a very strong magnetic field (B) of 10^5 T, which is one order of magnitude stronger than for the other studied molecules. The $k_{IC\text{-}M}$ contribution to the k_{IC} of isophlorin is small because most of its magnetic dipole transition moments between S_i and S_0 are equal to zero. The $k_{IC\text{-}M}$ contribution can be important in atomic spectroscopy[39,40] and in astrophysical studies of the interstellar medium,[41,42] of white dwarfs,[43,44] and of neutron stars at different stages of their existence.[45]

We also analysed the main acceptors of the electronic excitation energy both in the absence and the presence of an electric or a magnetic field. The acceptors are shown with ellipses in Fig. 1–3. Where one sees that the number of X-H acceptors increases when the molecules are exposed to an external electric field. In case of **ISO**, all X–H bonds become good acceptors when the molecule is exposed to an electric field. Substitution of the X–H bonds can either increase or decrease k_{IC} because some X–H bonds may be good acceptors in the presence of an external field and others are good acceptors in the absence of the field.

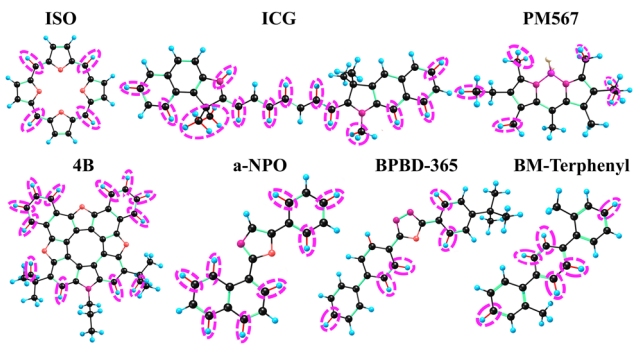

Fig. 1 The main acceptors of the energy of the S_1 state in the IC process in the absence of the external electric field.

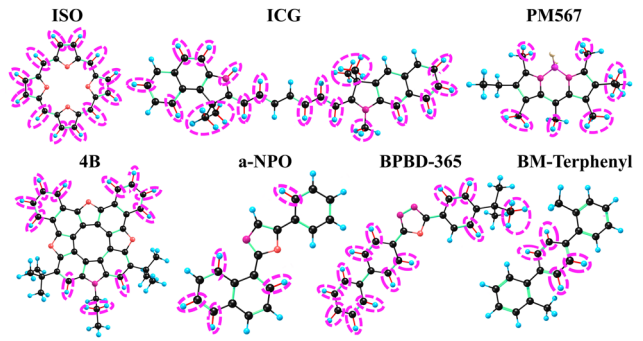

Fig. 2 The main acceptors of the energy of the S_1 state in the IC process in the presence of the external electric field.

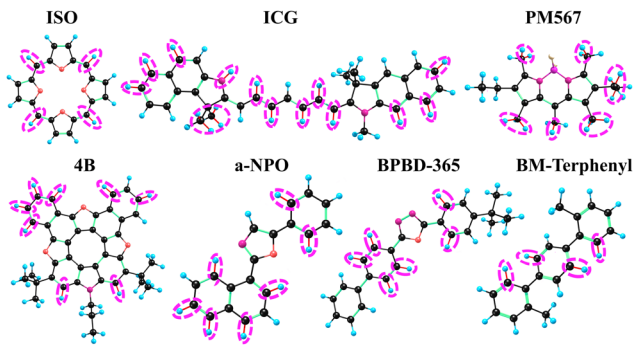

Fig. 3 The main acceptors of the energy of the S_1 state in the IC process in the absence of the external magnetic.

Summary and conclusion

The influence of external electric and magnetic fields on the k_{IC} for seven representative molecules was estimated using the theoretical model developed in this work. We showed that the electric-field contribution to the rate constant of internal conversion $k_{IC\text{-}E}$ at strong field strengths of 10^{11} V m^{-1} can generally become as large as the rate constant of internal conversion k_{IC} in the absence of the field. The present study showed that $k_{IC\text{-}E}$ for **ICG**, **4B**, and **PM** is as large as k_{IC} at a field strength of about 10^9 V m^{-1}, which may affect the photophysical properties of **ICG** derivatives that are widely used in plasmonic enhancement fluorescence[7] and of **PM** derivatives that are used in lasing processes.[21] The electric fields of plasmons or the electric field in strong laser-radiation experiments can reach this field strength. The electric-field effect can decrease the fluorescence quantum yield in such applications. The induced effect of an external magnetic field appears at very strong magnetic fields of 10^4–10^5 T. The magnetic-field contribution to the rate constant of internal conversion $k_{IC\text{-}M}$ can therefore be omitted in experiments on Earth. However, the magnetic-filed contribution may become significant in astrophysical studies of molecules and chemical processes near neutron stars and white dwarfs, whose atmospheres are exposed to extreme magnetic fields.

The developed model also gives the opportunity to determine which X–H bonds accept the electronic excitation energy and how the number of acceptors changes due to the presence of an external field. For the studied molecules, the number of X-H acceptors increases when they are exposed to an external electric field. By substituting the X–H bonds, the induced electric-field effect on the internal conversion can either increase or decrease the rate constant because some X–H bonds can be good acceptors in the presence of an external field and others are good acceptors in the absence of the field.

When the external fields are strong, $k_{IC\text{-}E}$ and $k_{IC\text{-}M}$ that are obtained at the second order in perturbation theory can be compared to k_{IC}, which is obtained at first-order perturbation theory level, without violating the applicability condition of the perturbation theory because we deal with internal conversion processes of different physical nature. Thus, none of them serves as a correction to the other one in the sense of perturbation theory.

The developed model can be applied to organic or organometallic compounds that have X–H bonds. The X–H bond approximation can be applied to lots of molecules because such molecules are common. It cannot be applied to specific molecules without X–H bonds such as fullerenes, cyclocarbons

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or pure metallic clusters. We considered only 50 excited states in expression (9), which may limit the accuracy of the calculated rate constants because further contributions can occur when including higher electronic intermediate states in the calculation. However, these contributions are not expected to significantly affect the $k_{\text{IC-E}}$ and $k_{\text{IC-M}}$ contributions to the rate constants because the contribution from the last five (from the 46th to the 50th) electronic states is negligible for $k_{\text{IC-E}}$ and $k_{\text{IC-M}}$.

In strong external magnetic fields, the zero-field splitting of triplet states increase. The energy gap between the S_1 state and energetically lower triplet states will decrease. Therefore, the influence of the external magnetic field on the intersystem crossing (ISC) process can increase and may appear at a weaker magnetic field than for IC. The acceptors modes of the ISC process are mainly C–C bonds with vibrational energies of $\sim$1400 cm^{-1} in the Franck–Condon approximation and the out-of-plane modes with vibrational energies of 400–600 cm^{-1} in the Herzberg–Teller approximation.[14,46] Therefore, the approximation considering only X–H bonds is not expected to work well for ISC processes.

Author contributions

Rashid Valiev suggested the theory and the algorithms. Rashid Valiev and Rinat Nasibullin implemented the algorithms and carried out the quantum chemical calculations. All authors contributed by participating in the discussion of the results and writing the manuscript.

Conflicts of interest

There are no conflicts to declare.

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