Near-infrared $^{2}E_{g} \rightarrow ^{4}A_{2g}$ and visible LMCT luminescence from a molecular bis-(tris(carbene)borate) manganese(IV) complex

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Near-infrared $^2E_g \rightarrow ^4A_{2g}$ and visible LMCT luminescence from a molecular bis-
(tris(carbene)borate) manganese(IV) complex

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Abstract: The molecular bis-(tris(carbene)borate) manganese(IV) complex [{PhB(MeIm)$_3$}$_2$Mn](OTf)$_2$ shows $^2$E$_g$ $\rightarrow$ $^4$A$_{2g}$ luminescence at 828 nm in the solid state, longer in wavelength by approximately 100 nm than typically observed for manganese(IV) and chromium(III) doped solids and for molecular chromium(III) complexes. Weak luminescence is also observed from a LMCT excited state with an absorption maximum at 500 nm. This represents the first molecular manganese(IV) compound for which luminescence has been reported.

Key words: six-coordinate manganese(IV) complexes, d$^3$ electron configuration, luminescence spectra, spin-flip luminescence, LMCT luminescence.

Résumé : Le complexe du manganèse(IV) [{PhB (MeIm)$_3$}$_2$Mn](OTf)$_2$ montre une bande de luminescence à 828 nm, correspondant à la transition $^2$E$_g$ $\rightarrow$ $^4$A$_{2g}$. Cette longueur d'onde est plus élevée d'environ 100 nm que ce qui est typiquement observé pour le manganèse(IV) et le chrome(III) dopés dans des réseaux de fluorure et d’oxyde ainsi que pour des complexes moléculaires du chrome(III). Une bande de luminescence faible est également observée à partir d'un état excité TCLM avec un maximum d'absorption à 500 nm. Il s’agit du premier exemple de luminescence d’un complexe moléculaire de manganèse(IV).

Mots clés : complexes hexacoordinés du manganèse(IV), configuration électronique d$^3$, spectres de luminescence, transitions intraconfigurationnelles, transitions TCLM.
Introduction

New first-row transition metal complexes with red to near-infrared (NIR) luminescence are of current interest for many areas of optical technology.\textsuperscript{1-4} An important recent example is the “molecular ruby analogue” complex, $\text{[Cr(N,N'-dimethyl-}N,N'\text{-dipyridine-2-ylpyridine-2,6-diamine)}_2]^{3+}$ ($\text{[Cr(ddpd)}_2]^{3+}$), with R-line ($^2E_g \rightarrow ^4A_{2g}$, idealized $O_h$ point group symmetry labels) emission at 775 nm, characteristic for chromium(III) with the d$^3$ electron configuration.\textsuperscript{3} The analogy is inspired by ruby with its brightly luminescent [CrO$_6$]$^{9-}$ luminophores, a unique material which continues to be the testing ground for many ideas and concepts of modern solid-state spectroscopy.\textsuperscript{5,7} Many other efficient luminescent solids based on chromium(III) centers are known.\textsuperscript{5-10} In contrast, there are far fewer luminescent materials containing the isoelectronic manganese(IV) ion,\textsuperscript{11-12} but recently many reports on manganese(IV) doped solids as efficient deep red emitters have been published.\textsuperscript{4,13-16} Such materials are also attractive because of the high abundance of manganese in the Earth's crust relative to more established deep-red emitting materials, often based on lanthanide ions.

The luminescence properties of molecular manganese(IV) compounds have received little interest and, to the best of our knowledge, no luminescence spectra have been been reported to date. These compounds are of interest to potentially extend the luminescence wavelength range of d$^3$ luminophores. As part of a larger effort on the coordination chemistry of “scorpionate” tris(carbene)borate chelating ligands,\textsuperscript{17-22} Smith and co-workers reported a manganese(IV) complex, [{PhB(MeIm)$_3$)$_2$Mn](OTf)$_2$, where PhB(MeIm)$_3$ is the phenyltris(3-methylimidazol-2-yl)borate anion, which was obtained by aerobic oxidation of the manganese(I) complex [{PhB(MeIm)$_3$}Mn(CO)$_3$].\textsuperscript{23} This complex can also be prepared by two electron oxidation of the homoleptic Mn(II) complex [{PhB(MeIm)$_3$)$_2$Mn]. Its structure is illustrated in Scheme 1. This
air-stable manganese(IV) complex exhibits an intense color, which prompted us to investigate its luminescence properties.

**Experimental Section**

The synthesis of \(\{\text{PhB(MeIm)}_3\}_2\text{Mn}(\text{OTf})_2\) is published and the compound has been characterized by X-ray diffraction, elemental analysis, UV-Vis absorption spectroscopy, solution magnetometry and mass spectrometry.\(^{23}\) The coordination geometry of the manganese(IV) center is approximately octahedral with exact inversion symmetry. Solution absorption spectra were measured in DMSO with a Cary 6000i spectrometer. Luminescence and Raman spectra were measured with a Renishaw Invia microscope at temperatures ranging from 85 K to 325 K with 488 nm excitation. Luminescence lifetimes were measured using 532 nm excitation pulses from a Nd:YAG laser.\(^{24}\) EPR and MCD instrumentation are described in the Supplementary Material.

**Results**

Fig. 1 shows luminescence spectra of crystalline \(\{\text{PhB(MeIm)}_3\}_2\text{Mn}(\text{OTf})_2\) at variable temperature. The overall luminescence intensity decreases with increasing temperature, but luminescence persists at room temperature. The most prominent luminescence feature is a band with a maximum at 828 nm at 85 K, shifting to 814 nm at room temperature. A second, weaker and broad luminescence band is observed in the 600 nm to 750 nm region. The lifetimes of the two bands are 1.5 µs (820 nm) and 50 ns (600 nm), clearly indicating that the two bands correspond to different electronic transitions.
The luminescence band at 828 nm has a width of between approximately 800 cm\(^{-1}\) and 2000 cm\(^{-1}\), broadening from 85 K to room temperature. The maximum of this band shifts to higher energy by 0.8 cm\(^{-1}\)/K, as shown in the inset to Fig. 1. This shift is on the expected order of magnitude for vibronic intensity gain in centrosymmetric transition metal complexes.\(^{25}\) Spectra plotted to match intensity of the highest band are given in Fig. S1 (Supplementary Material). The comparison clearly shows that the broadening occurs on the high-energy side, as expected for vibronic intensity gain.

The solution absorption spectrum of \([\{\text{PhB(MeIm)}_3\}_2\text{Mn}\}(\text{OTf})_2\)^{23} is distinctly different from the typical spectra of octahedral 3d\(^3\) complexes. The spectrum shows a broad band with a maximum at 500 nm and a molar absorptivity of approximately 8000 M\(^{-1}\) cm\(^{-1}\), more intense than spin-allowed d-d transitions\(^{26,27}\) by almost three orders of magnitude, masking any interconfigurational bands in this wavelength region. Similar intensities and wavelengths of band maxima were reported for the tris(pyrazolyl)borate complex, \([\text{Tp}^*\text{Mn}]\text{(ClO}_4\text{)}_2\) (\text{Tp}^*\text{=}hydrido(3,5-dimethylpyrazol-1-yl)borate anion), which exhibits intense bands at 599 nm and 549 nm (\(\varepsilon = 12000\) M\(^{-1}\) cm\(^{-1}\)).\(^{28}\) The inability to observe any d-d transitions precludes an analysis of the ligand-field experienced by the Mn(IV) ion in \([\{\text{PhB(MeIm)}_3\}_2\text{Mn}\}(\text{OTf})_2\), in contrast to that performed in detail for the related Cr(III) complex \([\text{Tp}_2\text{Cr}]\text{(ClO}_4\text{)}_2\),\(^{29}\) and to some extent for the related Mn(III) complexes \([\text{Tp}_2\text{Mn}]\text{(SbF}_6\text{)}, \ [\text{Tp}^*\text{Mn}]\text{(SbF}_6\text{)}, \text{ and } [\{\text{PhB(MeIm)}_3\}_2\text{Mn}]\text{(CF}_3\text{SO}_3\text{)}\).\(^{17,30}\) The MCD spectra in Fig. S3 (Supplementary Material) do not allow an unambiguous assignment of d-d transitions.

In contrast to the \(S = 1\) Mn(III) complex, \([\{\text{PhB(MeIm)}_3\}_2\text{Mn}]\text{(CF}_3\text{SO}_3\text{)}\), which is EPR-silent under conventional fields and frequencies due to its large zero-field splitting (ZFS),\(^{17}\) the \(S = 3/2\) Mn(IV) complex, \([\{\text{PhB(MeIm)}_3\}_2\text{Mn}]\text{(OTf)}_2\), is EPR active at both X-band
(\sim 9.3 \text{ GHz}) \text{ and Q-band (35 GHz) frequencies in 1:1 (v/v) acetonitrile/toluene frozen solution. These EPR spectra are presented in Figures S4 and S5 (Supplementary Material). The axial ZFS estimated for } \left[ \{ \text{PhB(MeIm)}_3 \}_2 \text{Mn} \right]^{2+} \text{ under these conditions is } |D| \approx 0.2 \text{ cm}^{-1}, \text{ which was validated computationally (Supplementary Material) and is consistent with values seen for six-coordinate complexes of Cr(III) }^{32-35} \text{ and Mn(IV).}^{31,36-39} \text{ This result indicates that there is nothing unusual about the spin quartet ground state of the title complex.}

**Discussion**

Wavelengths of the $^2E_g \rightarrow ^4A_{2g}$ luminescence maxima are given in Table 1 for manganese(IV) and chromium(III) ions in oxide and fluoride lattices, and for selected molecular compounds. Luminescence maxima for chromium(III) doped into fluoride and oxide lattices range from 660 nm to 720 nm for the examples given here. Manganese(IV) luminescence maxima in doped lattices range from 620 nm to 720 nm. The comparison reveals that the fluorides show maxima at shorter wavelengths than the oxides, and maxima for manganese(IV) species are at shorter wavelengths than those of chromium(III) in analogous environments. For example, Al$_2$O$_3$:Mn$^{4+}$ has a luminescence maximum at a wavelength shorter by 20 nm than the corresponding transition of ruby (Al$_2$O$_3$:Cr$^{3+}$). The molecular chromium(III) complexes in Table 1 show luminescence maxima over a significantly broader wavelength range, up to 775 nm, extending the range of chromium(III) in doped lattices to longer wavelength. Even so, the molecular manganese(IV) complex studied here emits at a wavelength longer by 40 nm than the longest wavelength maximum observed for any chromium(III) species considered here, despite the generally shorter wavelengths for manganese(IV) doped lattices. This comparison illustrates that the wavelength variation possible for manganese(IV) is seemingly even greater than that of
chromium(III).

The $^2E_g$ excited state in an octahedral coordination geometry arises from the $^2G$ term of the free ion with d$^3$ configuration. Ratios of the $^2E_g \rightarrow ^4A_{2g}$ transition energy in the doped solids and complexes to the free ion term energies have been calculated,$^{26}$ and are also collected in Table 1 as the parameter $\beta$. The lowering of the transition energy in the complex is predominantly due to the nephelauxetic effect, and so a reduction in the magnitude of $\beta$ can be used to infer more significant covalent metal-ligand bonding.$^{40}$ To demonstrate the anticipated range of $\beta$, values for the NIR spin-flip transition of vanadium(III) ions (d$^3$ configuration) doped into halide lattices are 0.96, 0.89 and 0.86 for fluoride, chloride and bromide lattices, respectively.$^{41}$ For the doped oxides and fluorides, the manganese(IV) species consistently show lower $\beta$ values than those incorporating chromium(III) centers with similar ligands. For the free ions, the ionic radii of chromium(III) and manganese(IV) are 0.62 Å and 0.53 Å, respectively.$^{42}$ The smaller manganese(IV) therefore shows a higher-energy free ion $^2G$ term since the repulsive effects are more significant. In the doped solids, however, the smaller manganese(IV) ion forms longer covalent bonds with the lattice than does the chromium(III) ion, giving a reduction in electronic repulsion through greater delocalization of electron density and consequently showing a more significant reduction in transition energy, leading to lower $\beta$ values.

To shift emission into the desirable NIR range, systems must exhibit low $\beta$ values. Chromium(III) molecular compounds have lower $\beta$ values than doped lattices, although for the examples here, the lowest value of $\beta$ is only 0.88. Interestingly, the manganese(IV) doped solids possess lower $\beta$ values than comparable chromium(III) systems; for doped Al$_2$O$_3$, manganese(IV) shows a $\beta$ value of 0.86, lower than ruby with a value of 0.99. For reference, the
β value for vanadium(III) doped into Al₂O₃ is 0.92,⁴³ indicating that there are no straightforward trends relating ionic radii or formal charges of the transition metal center to the β parameter. For further context, we may also compare with the sequence of d⁲ configured tetrahedral MO₄ luminophores [CrO₄]⁴⁻, [MnO₄]³⁻, and [FeO₄]²⁻, which show ¹E → ³A₂ spin-flip luminescence.⁴⁴ Despite the monotonic increase in the energy of the corresponding free-ion terms throughout the series, the luminescence energies of the chromium and manganese species are roughly equal, and the iron species shows a significantly lower energy. The β values as calculated using the same approach as above are 0.66 for chromium(IV), 0.57 for manganese(V), and 0.38 for iron(VI), the latter of which in particular is dramatically lower than the value for [{PhB(MeIm)₃}₂Mn]²⁻. This comparison shows that luminescence from molecular manganese(IV) systems can occur further into the NIR, as the title complex illustrates.

The ligands of the title complex are very strong σ-donors, an important property for obtaining intense luminescence used for the design of the molecular ruby analogue [Cr(ddpd)₂]³⁺.³ The resulting significant delocalization of the manganese(IV) d-electrons away from the free ion orbitals reduces the spin-flip transition energy and leads to a low value of β. The strong ligand-field leads to high-energy interconfigurational d-d transitions, but none of these bands can be observed in the absorption spectrum due to the broad and intense band centered at 500 nm. MCD spectra are shown in Fig. S3 (Supplementary Material). Their resolved structure can not be unambiguously assigned and does not provide evidence for d-d transitions.

The weak luminescence band between 650 nm and 750 nm in Fig. 1 is compared to the absorption spectrum in Fig. 2. The luminescence band shows barely resolved vibronic structure with three peaks separated by approximately 1200 cm⁻¹. This frequency interval corresponds to
modes located on the ligands, as metal-ligand modes are typically observed at much lower frequencies. The high molar absorptivity of the absorption band and the magnitude of the vibronic spacing support an LMCT assignment.

In order to more quantitatively probe the relationship between the two experimental bands observed in Fig. 2, spectra have been calculated using a time-dependent approach. In this method, the initial and final states are described by harmonic potentials with identical force constants defined by a single vibrational frequency $\omega_k$ for the ground and excited states. These potentials are offset along normal coordinate $Q_k$ by the dimensionless parameter $\Delta Q_k$, which is effectively the extent of perturbation of the ground state geometry along a particular vibrational coordinate. Fig. 3 shows a schematic view of this model with parameters identified.

At time $t_0$, the initial wavepacket $\phi$ is moved vertically to the final state surface, where it is allowed to propagate. The overlap integral is then evaluated between the wavepacket at $t_0$ and the wavepacket at $t$. This is referred to as the autocorrelation function, $\langle \phi | \phi(t) \rangle$ given along coordinate $k$ by:

$$\langle \phi_k | \phi_k(t) \rangle = \frac{\Delta Q_k^2}{2} (1 - e^{-i\omega_k t})$$

In some cases, including the present situation, a single vibrational mode is insufficient to adequately approximate the potential energy surfaces. When this arises, assuming that there is no coupling between modes, individual autocorrelation functions are appraised along each relevant normal coordinate, and the overall autocorrelation function is found by taking the product of these;
where $E_{00}$ is the electronic origin, here estimated from the crossing point of the absorption and luminescence spectra shown in Fig. 2. $\Gamma$ is a phenomenological damping factor which dissipates the amplitude of the wavepacket over time. The parameters $\Delta Q_k$ cannot be determined experimentally, and so are treated as adjustable parameters in the model—the same is true for $\Gamma$, which chiefly determines the overall resolution of the individual peaks in the frequency domain. The Fourier transform of the overall autocorrelation function multiplied by the frequency cubed $\omega^3$ of emitted light (or the frequency $\omega$ of applied light for absorption) directly provides the frequency domain spectrum; 

\[
I(\omega) = \omega^3 \int_{-\infty}^{\infty} e^{-i\omega t} \langle \phi(t) \rangle d(t)
\]

(3)

To test the idea that the luminescence and absorption bands in Fig. 2 are related, both bands were fitted simultaneously using a least squares fitting routine. Experimental and calculated spectra are compared in Fig. 2. The vibrational frequencies used to describe the potentials were taken from the Raman spectra, recorded by excitation at 488 nm, shown in Fig. 2 and S2 (Supplementary Material). Since the excitation wavelength is close to the absorption band maximum at 500 nm, it is likely that some of these features are resonance enhanced, identifying the modes with highest $\Delta Q_k$ values. The most intense Raman peak is at 1350 cm$^{-1}$, and since a lower frequency mode is required to reproduce the spacing of $\sim 1200$ cm$^{-1}$ observed in the
luminescence spectrum, the most intense peak at a Raman shift lower than 1200 cm\(^{-1}\) is used.

The absorption spectrum does not show resolved vibronic structure and excited-state vibrational frequencies identical to those of the ground state were used for our calculations. In order to use a common value of \(E_{\text{00}}\) for both luminescence and absorption calculations, a third, lower-frequency mode is required. We use an initial value of 260 cm\(^{-1}\), a region common for M-L modes, with a value of 313 cm\(^{-1}\) resulting from the fit. All other values were floated and all parameter values are given in Table 2. The value of \(\Gamma\) was defined separately for each band. This model involves the lowest number of adjustable parameters necessary to fit the spectra in Fig. 2.

The calculated spectra in Fig. 2 are in very good agreement with the experimental data, reproducing luminescence and absorption bandshapes and also the Stokes shift of 4800 cm\(^{-1}\), a value significantly higher than for chromium(III) systems with luminescence from the \(^4T_{2g}\) excited state which commonly show Stokes shifts lower than 3000 cm\(^{-1}\), illustrated by the value of 2900 cm\(^{-1}\) in the fluoride lattice \(\text{Na}_3\text{In}_2\text{Li}_3\text{F}_{12}\) doped with chromium(III).\(^{47}\) The vibronic interval of \(~1200\) cm\(^{-1}\) observed in the luminescence spectrum does not correspond to an individual signal in the Raman spectrum, a situation referred to as the missing mode effect (MIME),\(^{48-50}\) but this structure is reproduced by our model. By comparison to calculated vibrational modes of imidazole,\(^{51}\) the two higher frequency modes used are in the typical range of in-plane ring-deformation modes, supporting the LMCT assignment of the absorption band.

The time-dependent picture shows the origin of the observed vibronic interval, resulting from combined wavepacket motion along two coordinates. Fig. 4 shows the absolute value of the autocorrelation functions for the two higher-frequency modes and for their product, defined with the parameters in Table 2. The recurrence \(t_2\) defines the vibronic spacing, the position of which is a result of the product of the individual autocorrelation functions. For one-dimensional models
calculated with $\omega_k = 1350 \text{ cm}^{-1}$ and $1080 \text{ cm}^{-1}$, $t_2$ is at 24 fs and 29 fs, respectively. When both of these frequencies are included in the model, $t_2$ occurs at an intermediate time of 26 fs. Converting these times to wavenumbers gives approximately the expected vibronic spacings, with the two-dimensional $t_2$ being at a frequency of ~1300 cm$^{-1}$, although, since there is also broadening of the calculated peaks due to $\Gamma$, this value does not correspond exactly to the structure observed in the calculated frequency domain spectrum.

The manganese(IV) complex [{PhB(MeIm)$_3$}$_2$Mn](OTf)$_2$ shows both NIR spin-flip and LMCT luminescence transitions due to the strong $\sigma$–donor character of the tris(carbene)borate ligands. Among 3d$^3$ ions, luminescence investigations of Cr(III) are much more common than of Mn(IV), and, to the best of our knowledge, the title complex is the first molecular manganese(IV) complex for which luminescence is reported. We suggest that Mn(IV) systems receive greater attention in this regard than has hitherto been the case.

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References


(52) Kramida, A.;Ralchenko, Y.; Reader, J.; NIST Atomic Spectra Database (ver. 5.3), [Online], National Institute of Standards and Technology, Gaithersburg, MD.
Figure captions

Scheme 1. Schematic structure of [{PhB(MeIm)}$_3$]$_2$Mn$^{2+}$

Figure 1. Luminescence spectra of [{PhB(MeIm)}$_3$]$_2$Mn](OTf)$_2$ at variable temperature with 488 nm excitation. Spectra have been corrected for system response. The inset shows the shift of the $^2E_g \rightarrow ^4A_{2g}$ band maximum with temperature.

Figure 2 Experimental luminescence (solid, 85 K), absorption (DMSO solution, room temperature) and calculated (dotted) LMCT luminescence and absorption bands. The 488 nm excitation wavelength $\lambda_{exc}$ is indicated, as are Raman shifts for two bands. Calculated luminescence and absorption bands were obtained with the fit procedure described in the Supplementary Material. The x symbols denote limits of the fit ranges. Parameter values resulting from the fit are given in Table 2

Figure 3. Schematic view of the luminescence transition in the model used to calculate the spectra in Fig. 2.

Figure 4. Absolute values of autocorrelation functions used to calculate absorption and luminescence spectra.
Table 1. Luminescence wavelengths of chromium(III) and manganese(IV) doped solids and molecular compounds (d³ electron configuration, idealized O₈ symmetry labels). β is calculated as the ratio of the energy of the ²E_g → ⁴A₂g transition to the energy of the corresponding transition in the Mn⁴⁺ and Cr³⁺ free ions, calculated as the average of the one-photon, j-allowed transitions, at 17192.4 cm⁻¹ and 14590.1 cm⁻¹, respectively.¹⁰

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¹ Average of R₁ and R₂ lines at 694.5 nm and 692.7 nm. ¹³
² Average of R₁ and R₂ lines at 14786 cm⁻¹ and 14866 cm⁻¹.¹¹
³ Average of R₁ and R₂ lines at 15116 cm⁻¹ and 15126 cm⁻¹.¹⁰
⁴ Average of R₁ and R₂ lines at 725.1 nm and 723.6 nm.¹⁰
⁵ Zero phonon line at 13826.8 cm⁻¹.⁸
⁶ From ⁴⁷
g 15045±2 cm\(^{-1}\) at ambient pressure and 4.2 K.\(^9\)

h Average of \(R_1\) and \(R_2\) lines at 622.08 nm and 621.70 nm.\(^4\)

i Zero phonon line at 620.5 nm.\(^5^{,}\)\(^4\)

j Zero phonon line at 16021 cm\(^{-1}\).\(^{55}\)

k Position of maximum reported as 667 nm in Table 1.\(^{56}\)

\(^1\) Reported in Table 1 as 13700 cm\(^{-1}\) for \([\text{Cr(phen)}_3]^{3+}\) and 13000 cm\(^{-1}\) for \([\text{Cr(tpy)}_2]^{3+}\).\(^{57}\)

\(^m\) \([\text{Cr}(N,N'-\text{dimethyl-}N,N'-\text{dipyridine-2-ylpyridine-2,6-diamine})_2]^{3+}\). Band maximum at 775 nm.\(^2\)

\(^n\) This work.
Table 2. Parameter values obtained from simultaneous fitting of luminescence and absorption spectra in Fig. 2. \( \omega_1 \) and \( \omega_2 \) are experimental Raman frequencies.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{00} ) (cm(^{-1}))</td>
<td>16844</td>
</tr>
<tr>
<td>( \Gamma ) (cm(^{-1}))</td>
<td>163 (lum.), 550 (abs.)</td>
</tr>
<tr>
<td>( \omega_1 ) (cm(^{-1})), ( \Delta Q_1 )</td>
<td>1080, 1.09</td>
</tr>
<tr>
<td>( \omega_2 ) (cm(^{-1})), ( \Delta Q_2 )</td>
<td>1350, 1.58</td>
</tr>
<tr>
<td>( \omega_3 ) (cm(^{-1})), ( \Delta Q_3 )</td>
<td>313, 2.18</td>
</tr>
</tbody>
</table>
Scheme 1

44x48mm (300 x 300 DPI)
Figure 1

180x183mm (300 x 300 DPI)
Figure 2

152x116mm (300 x 300 DPI)
Figure 3

157x133mm (300 x 300 DPI)
Figure 4

\( |\langle \phi | \phi(t) \rangle| \)

\( \omega_k = 1350 \text{ cm}^{-1} \)
\( \omega_k = 1080 \text{ cm}^{-1} \)

Two modes

Time (s)

0
20
40
60
80 \times 10^{-15}

165x155mm (300 x 300 DPI)