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Electronic Excited States of Tetracyanonickelate(II)

Patrick Hummel, Nicholas W. Halpern-Manners, and Harry B. Gray*

California Institute of Technology, Mail Code 139-74, Pasadena, California 91125

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We revisit the assignment of the absorption spectrum of tetracyanonickelate(II) by calculating energies of excitations with time-dependent density functional theory. Our results give strong evidence that the original assignment of the spectrum is only partially correct. We thus propose an alternative assignment consistent with our theoretical calculations and all available experimental evidence. In particular, we reassign the bands at 22 400 and 32 300 cm^{-1} to the $^1A_{1g} \rightarrow {}^3A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) and $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitations.

Introduction

The groundwork for the interpretation of the absorption spectrum of tetracyanonickelate(II) was laid out over 40 years ago.[1,2] Experimental observations combined with theoretical analyses provided a detailed description of both the ground and lowest excited states of square planar metal complexes. Thereafter, investigators used spectroscopic methods such as linear polarization and magnetic circular dichroism, as well as theoretical calculations, to lend further insights into the interpretation of the $Ni(CN)_4^{2-}$ spectrum.[3−15] Although other possibilities for the assignment of this spectrum were considered,[6,12] most investigations appeared to confirm the original interpretation.[10,11,13,15]

The absorption spectrum of $Ni(CN)_4^{2-}$ features a very weak band at 22 400 cm^{-1}, moderately intense bands at 23 000, 27 000, and 32 300 cm^{-1}, as well as two very intense bands at 35 200 and 37 600 cm^{-1}. It has been convincingly demonstrated by magnetic circular dichroism that the two intense bands correspond to the $^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g} \rightarrow a_{2u}$) and $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$) excitations, respectively.[7,9] Polarization studies provide strong evidence that the bands at 23 000 and 27 000 cm^{-1} correspond to the $^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$) and $^1A_{1g} \rightarrow {}^1A_{2g}$ ($e_g \rightarrow b_{1g}$) excitations. Last, the bands at 22 400 and 32 300 cm^{-1} have been assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) and $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) excitations, respectively, consistent with the energy ordering, $e_g(xz,yz) < a_{1g}(z^2) < b_{2g}(xy) \ll b_{1g}(x^2 - y^2)$.

The assignment of the 22 400 cm^{-1} band to the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation is dubious because the band has an extinction coefficient of 2 M^{-1} cm^{-1}, far less than the expected value for a spin-allowed excitation. In this paper, we use methods based on density functional theory (DFT) and time-dependent density functional theory (TDDFT) to revisit the assignment of the absorption spectrum of $Ni(CN)_4^{2-}$. Importantly, in accord with the generally accepted d-orbital energy ordering in square planar complexes containing π-acceptor ligands,[16−21] we find that the b_{2g} orbital lies ~1 eV lower in energy than the a_{1g} orbital, strongly suggesting that the original assignment of the bands cannot be completely correct. To rectify this situation, we assign the band at 22 400 cm^{-1} to the $^1A_{1g} \rightarrow {}^3A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation,

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* To whom correspondence should be addressed. E-mail: hbgray@caltech.edu.

(1) Gray, H. B.; Ballhausen, C. J. *J. Am. Chem. Soc.* **1963**, *85*, 260.
(2) Ballhausen, C. J.; Gray, H. B. *Molecular Orbital Theory*; W. A. Benjamin: New York, 1964.
(3) Gray, H. B. *Transition Met. Chem.* **1965**, *1*, 239.
(4) Ballhausen, C. J.; Bjerrum, N.; Dingle, R.; Eriks, K.; Hare, C. R. *Inorg. Chem.* **1965**, *4*, 514.
(5) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier Publishing Co.: Amsterdam, 1968.
(6) Mason, W. R., III; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5721.
(7) Stephens, P. J.; McCaffery, A. J.; Schatz, P. N. *Inorg. Chem.* **1968**, *7*, 1923.
(8) Dahl, J. P.; Dingle, R.; Vala, M. T. *Acta Chem. Scand.* **1969**, *23*, 47.
(9) Piepho, S. B.; Schatz, P. N.; McCaffery, A. J. *J. Am. Chem. Soc.* **1969**, *91*, 5994.
(10) Demuynck, J.; Veillard, A.; Vinot, G. *Chem. Phys. Lett.* **1971**, *10*, 522.
(11) Hillier, I. H.; Saunders, V. R. *Mol. Phys.* **1972**, *23*, 449.
(12) Cowman, C. D.; Ballhausen, C. J.; Gray, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 7873.
(13) Demuynck, J.; Veillard, A. *Theor. Chim. Acta (Berlin)* **1973**, *28*, 241.
(14) Anex, B. G.; Musselman, R. L. *J. Phys. Chem.* **1980**, *84*, 883.
(15) Sano, M.; Kashiwagi, H.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 750.
(16) Isci, H.; Mason, W. R. *Inorg. Chem.* **1975**, *14*, 905.
(17) Isci, H.; Mason, W. R. *Inorg. Chem.* **1975**, *14*, 913.
(18) Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J., Jr.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485.
(19) Geoffroy, G. L.; Isci, H.; Litrenti, J.; Mason, W. R. *Inorg. Chem.* **1977**, *16*, 1950.
(20) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G. II. *Inorg. Chem.* **1978**, *17*, 828.
(21) Smith, D. C.; Miskowski, V. M.; Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1990**, *112*, 3759.

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and the band at 32 300 cm^{-1} to the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation. We thus propose an interpretation consistent with these TDDFT calculations, as well as all available experimental evidence. Our assignment is different from any assignment previously considered in the literature.

Computational Methods

All calculations reported herein were performed with the TURBOMOLE program package for ab initio electronic structure calculations.[22] We used the TZVP basis set[23] for all atoms in calculating the properties of $Ni(CN)_4^{2-}$. We performed four different DFT calculations, each using a different exchange-correlation functional selected from B3LYP, PBE, BP86, and BLYP.[24−32] The calculations were done using the COSMO continuum solvation model[33] for treatment of solvation effects with a dielectric constant of 37.5. Each of the four calculations was performed with an m3 gridsize.[34] The calculated geometry of $Ni(CN)_4^{2-}$ was optimized using TURBOMOLE's JOBEX program with generalized internal coordinates[35] and the corresponding STATPT module. Energies of well-converged ground-state molecular orbitals were calculated with the DSCF module for semi-direct self-consistent-field evaluation. We then used these ground-state molecular orbitals to calculate the energies of the low-lying singlet → singlet transitions and singlet → triplet transitions with the ESCF package for full TDDFT calculations.[36,37] Similar methods in TURBOMOLE have previously been used to successfully investigate the electronic structures and absorption spectra of various inorganic complexes.[38−41]

Results and Discussion

We have calculated the ground-state properties and the energies of the low-lying excitations for $Ni(CN)_4^{2-}$ using the B3LYP, BLYP, BP86, and PBE exchange−correlation functionals. The results are given in Tables 1−3.

Table 1. Calculated and Crystal Structure Interatomic Distances (Å) for $Ni(CN)_4^{2-}$ [a]

	B3LYP	B-LYP	B−P	PBE	crystal structure
Ni−C	1.889	1.886	1.864	1.863	1.860
C−N	1.161	1.173	1.174	1.174	1.154

[a] Calculated bond distances are in good agreement with the crystal structure.

Table 2. Calculated Energies (eV) of the Frontier Orbitals in $Ni(CN)_4^{2-}$

orbital	B3LYP	B-LYP	B−P	PBE
$b_{2g}(xy)$	−7.42	−5.77	−6.05	−5.90
$e_g(xz,yz)$	−6.75	−5.11	−5.43	−5.29
$a_{1g}(z^2)$	−6.38	−4.74	−5.06	−4.91
$b_{1g}(x^2 - y^2)$	−0.41	−1.55	−1.63	−1.48
$a_{2u}(\pi^*)$	−0.49	−1.19	−1.51	−1.39

Table 3. Calculated and Experimental Energies (cm^{-1}) of the Low-Lying Electronic Excitations in $Ni(CN)_4^{2-}$ [a]

excitation	expt	B3LYP	B-LYP	B−P	PBE
$^1A_{1g} \rightarrow {}^3B_{1g}$ ($a_{1g} \rightarrow b_{1g}$)		16 100	21 400	23 300	23 400
$^1A_{1g} \rightarrow {}^3E_g$ ($e_g \rightarrow b_{1g}$)		19 700	24 600	26 600	26 800
$^1A_{1g} \rightarrow {}^3A_{2g}$ ($b_{2g} \rightarrow b_{1g}$)	22 400	26 100	29 900	31 600	31 800
$^1A_{1g} \rightarrow {}^3A_{2u}$ ($a_{1g} \rightarrow a_{2u}$)		34 100	27 200	26 500	26 600
$^1A_{1g} \rightarrow {}^3E_u$ ($e_g \rightarrow a_{2u}$)		37 400	30 500	30 200	30 200
$^1A_{1g} \rightarrow {}^3B_{1u}$ ($b_{2g} \rightarrow a_{2u}$)		44 000	36 400	36 000	35 800
$^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$)	23 000	26 500	30 000	32 100	32 200
$^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$)	27 000	28 800	31 600	33 600	33 800
$^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$)	32 300	31 600	34 000	36 000	36 100
$^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g} \rightarrow a_{2u}$)	35 200	38 300	30 600	30 500	30 300
$^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$)	37 600	40 900	33 200	33 300	33 200
$^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$)		45 100	37 000	36 700	36 500

[a] B3LYP gives the best agreement with experiment.

All calculated ground-state bond distances are in good agreement with the crystal structure,[42] but we find that B3LYP gives the best quantitative agreement with the experimentally observed excitation energies. To ensure the reliability of our study, our explanation of the correct assignment of the absorption spectrum will depend only on results that hold for each of the four exchange−correlation functionals considered.

There are six observed peaks in the spectrum (Figure 1). The second (23 000 cm^{-1}), third (27 000 cm^{-1}), fifth (32 300 cm^{-1}), and sixth (35 200 cm^{-1}) features were originally assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$), $^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$), $^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g} \rightarrow a_{2u}$), and $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$) excitations, respectively. Analyses of polarization and magnetic circular dichroism data indicate that the assignments for these four bands are correct.[4,7,9,12] Thus, we focus on the interpretation of the first and fourth observed peaks in the spectrum.

The original assignments of the first (22 400 cm^{-1}) band to the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation and the fourth (32 300 cm^{-1}) band to the $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) excitation have several problems. One is that the first band has an extinction coefficient (2 M^{-1} cm^{-1}) that falls well below the range for spin-allowed ligand-field transitions For example, in octahedral metal cyanide complexes, where the assignments are well established, the intensities of the spin-allowed ligand-field transitions are typically on the order of 100−1000 M^{-1} cm^{-1}.[43] Additionally, in the present complex, the

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[22] Ahlrichs, R.; Bär, M.; Baron, H. P.; Bauernschmitt, R.; Böcker, S.; Deglmann, P.; Ehrig, M.; Eichkorn, K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Horn, H.; Hättig, C.; Huber, C.; Huniar, U.; Kattannek, M.; Köhn, A.; Kölmel, C.; Kollwitz, M.; May, K.; Ochsenfeld, C.; Öhm, H.; Patzelt, H.; Rubner, O.; Schäfer, A.; Schneider, U.; Sierka, M.; Treutler, O.; Unterreiner, B.; von Arnim, M.; Weigend, F.; Weis, P.; Weiss, H. *TURBOMOLE V5−7*; Quantum Chemistry Group, University of Karlsruhe: Karlsruhe, Germany, 2004.

[23] Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

[24] Dirac, P. A. M. *Proc. R. Soc. (London) A* **1929**, *123*, 714.

[25] Slater, J. C. *Phys. Rev.* **1951**, *81*, 385.

[26] Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

[27] Perdew, J. P.; Wang, Y. *Phys. Rev. B.* **1992**, *45*, 13244.

[28] Becke, A. D. *Phys. Rev. A.* **1988**, *38*, 3098.

[29] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.

[30] Perdew, J. P. *Phys. Rev. B.* **1986**, *33*, 8822.

[31] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

[32] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[33] Klamt, A.; Schürmann, G. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 799.

[34] Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346.

[35] von Arnim, M.; Ahlrichs, R. *J. Chem. Phys.* **1999**, *111*, 9183.

[36] Furche, F. *J. Chem. Phys.* **2001**, *114*, 5982.

[37] Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117*, 7433.

[38] Hummel, P.; Oxgaard, J.; Goddard, W. A., III; Gray, H. B. *J. Coord. Chem.* **2005**, *58*, 41.

[39] Hummel, P.; Oxgaard, J.; Goddard, W. A., III; Gray, H. B. *Inorg. Chem.* **2005**, *44*, 454.

[40] Hummel, P.; Winkler, J. R.; Gray, H. B. *Dalton Trans.* **2006**, *1*, 168.

[41] Hummel, P.; Gray, H. B. *Coord. Chem. Rev.*, in press.

[42] Larsen, F. K.; Hazell, R. G.; Rasmussen, S. E. *Acta Chem. Scand.* **1969**, *23*, 61.

[43] Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260.

Table 4. Assignments of the Electronic Transitions in the Absorption Spectrum of $Ni(CN)_4^{2-}$ [a]

energy (cm^{-1})	ϵ (M^{-1} cm^{-1})	original assignment	current assignment
22 400	2	$^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$)	$^1A_{1g} \rightarrow {}^3A_{2g}$ ($b_{2g} \rightarrow b_{1g}$)
23 000	50	$^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$)	$^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$)
27 000	100	$^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$)	$^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$)
32 300	700	$^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$)	$^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$)
35 200	4 200	$^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g} \rightarrow a_{2u}$)	$^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g} \rightarrow a_{2u}$)
37 600	10 600	$^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$)	$^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$)

[a] Current and original assignments differ for the bands at 22 400 and 32 300 cm^{-1}.

spin-allowed ligand-field bands both have intensities on the order of 100 M^{-1} cm^{-1}. If the first band were due to a spin-allowed transition, we would expect to observe a similarly large intensity. Thus, the assignment of the 22 400 cm^{-1} band to the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation is unlikely.

The assignment of the lowest-lying band to the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation was in part based on the assumption that the metal orbitals follow the energy ordering $e_g(xz,yz) < a_{1g}(z^2) < b_{2g}(xy) \ll b_{1g}(x^2 - y^2)$.[1,3] However, the ground-state orbital energies we have presently calculated are quite different. In accord with work on related square planar complexes containing π-acceptor ligands,[16−21] we find that the correct ordering of the d orbitals is $b_{2g}(xy) < e_g(xz,yz) < a_{1g}(z^2) \ll b_{1g}(x^2 - y^2)$ and that the $b_{2g}(xy)$ orbital falls ~1 eV lower in energy than the $a_{1g}(z^2)$ orbital. This ordering reflects the importance of $d_{xy} \rightarrow \pi^*(CN)$ back-bonding in stabilizing the $b_{2g}(xy)$ orbital.

The original assignment of the spectrum requires the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) transition to fall ~5000 cm^{-1} lower in energy than the $^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$) excitation and the $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) to fall ~5000 cm^{-1} lower in energy than the $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$) excitation. By contrast, the TDDFT calculations reported here suggest that the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation is ~3000 cm^{-1} higher in energy than the $^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$) transition and the $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) transition is ~3000 cm^{-1} higher in energy than the $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$) excitation. These results are incompatible with the original assignment.

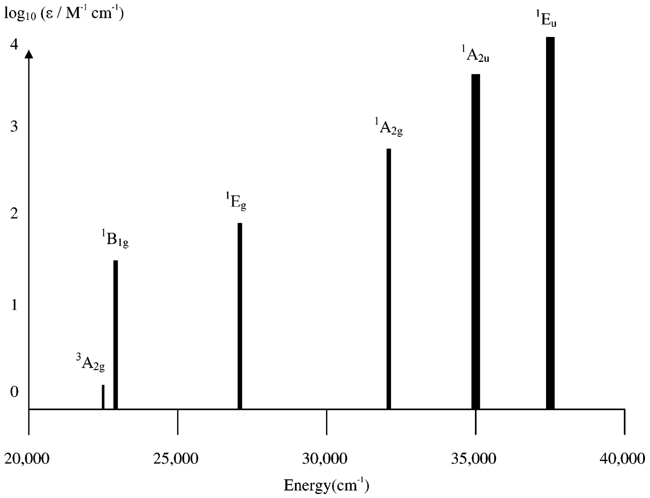

Figure 1. Peak positions and extinction coefficients (ϵ) in the absorption spectrum of $Ni(CN)_4^{2-}$. Thick lines correspond to allowed excitations, intermediate lines correspond to spin-allowed but orbitally forbidden transitions, and the thin line corresponds to a spin and orbitally forbidden transition.

Given the incompatibility of the original assignment with the present theoretical calculations, we now suggest an assignment consistent with our theoretical calculations and all available experimental evidence. Since the TDDFT calculations place the $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) transition at higher energy than the $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$) excitation, we seek to place the $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) excitation at higher energy than the peak corresponding to the $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$) excitation. There are no bands higher in energy within 13 000 cm^{-1} of the peak corresponding to $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$). However, since we expect the intensity of the orbitally forbidden $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) transition to be much less than that of the broad, orbitally allowed $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$) band, it would not be surprising for $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) to be overshadowed by the $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$) absorption. Thus, we conclude that the $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) transition is not observed in the absorption spectrum.

Since the peak at 32 300 cm^{-1} does not correspond to the $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$) transition, it must be reassigned. The 32 300 cm^{-1} band has intensity comparable to that of the other bands attributed to spin-allowed ligand-field excitations. Thus, we expect this band to correspond to a spin-allowed but orbitally forbidden excitation. The only spin-allowed transition that has not been properly assigned is the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation. This excitation is expected to lie roughly 3000 cm^{-1} higher in energy than the band corresponding to the $^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$) transition, in good agreement with the observed peak at 32 300 cm^{-1}. Furthermore, given that the band cannot be assigned to $^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$), there appears to be no other reasonable alternative. Thus, we assign the feature at 32 300 cm^{-1} to the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation.

Last, we turn our attention to the 22 400 cm^{-1} peak. The weak intensity of the peak suggests that it arises from a spin-forbidden excitation. This feature in the spectrum lies very slightly below the peak corresponding to the $^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$) excitation. Our TDDFT calculations indicate that $^1A_{1g} \rightarrow {}^3A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) is only slightly lower in energy than the $^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$) excitation, whereas the other spin-forbidden ligand-field excitations lie far lower. Additionally, our calculated singlet−triplet energy separations for the ligand-field excitations suggest that only $^1A_{1g} \rightarrow {}^3A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) could lie as high as 22 400 cm^{-1}. Thus, we assign the 22 400 cm^{-1} band to the $^1A_{1g} \rightarrow {}^3A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) excitation. Our complete assignment of the absorption spectrum is summarized in Table 4.

Conclusion

The results presented here give strong evidence that the original assignment of the $Ni(CN)_4^{2-}$ absorption spectrum is only partially correct. We find that the correct ordering of the energies of the d orbitals in $Ni(CN)_4^{2-}$ is $b_{2g}(xy) < e_g(xz,yz) < a_{1g}(z^2) \ll b_{1g}(x^2 - y^2)$. We have reassigned two of the peaks in the absorption spectrum to accommodate all available experimental and theoretical evidence.

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