# "Almost Delocalized" Intervalence Compounds

## Stephen F. Nelsen*[a]

**Abstract:** Interest is high in $^+$M – bridge – M systems that have very low barriers to intramolecular electron transfer giving M – bridge – M$^+$ ("almost delocalized" systems). Hush showed how to evaluate the electronic coupling across the bridge ($H$) from the M-to-M charge-transfer optical absorption band, but did not point out that his classical model causes the extinction coefficient to suddenly drop to zero at a photon energy of $2H$. Ignoring this band cutoff leads to a low estimation of $H$.

**Keywords:** electron transfer · hush theory · intervalence compounds · radical ions

## Introduction

Intervalence compounds have two charge-bearing units (**M**) connected by a "bridge" (**B**), and are at an oxidation state that could place charges that differ by one on the **M** units. The concept was developed for compounds that have transition metal coordination complexes as **M**, and one bidentate ligand linking the two **M** units, so it serves as **B**. Examples of **B** discussed here are shown in Scheme 1. Robin and Day classified intervalence compounds according to the size of
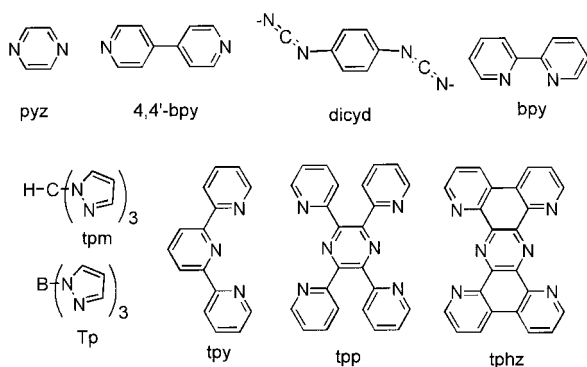


Scheme 1. Ligands for intervalence compounds with transition metal centers.

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the electronic interaction between the **M** groups, the off-diagonal matrix element $H$ (defined below; also called $J$, $V$, and $\beta$).[1] Class I compounds have complete charge localization (and may be abbreviated $^n$**MBM**$^{n+1}$), and $H = 0$; intramolecular electron transfer (ET) between their **M** groups will not occur. Class II compounds still have different **M** groups and are abbreviated $^n$**MBM**$^{n+1}$, but they have detectable electronic interaction that partially mixes the character of the oxidized and reduced **M** units through interaction with the bridge orbitals. They are the simplest systems that have been devised for considering electron transfer (ET), and have been important in the development of ET theory.[2, 3] Class III compounds have such a large $H$ that delocalization occurs, and the formal charge on each **M** group is $n + \frac{1}{2}$. Hush devised a simple theoretical analysis of the optical spectra of Class II intervalence compounds that also has had lasting significance.[2] The energy surface for thermal ET is obtained from a two-state classical model in which the electronic interaction between diabatic surfaces (those at $H = 0$; they would be those occupied for a Class I compound) is the off-diagonal matrix element $H$ in a $2 \times 2$ secular determinant [Eq. (1)]. Solution gives the adiabatic energy surfaces,

$$\begin{vmatrix} H_0 - E & H \\ H & H_1 - E \end{vmatrix} = 0 \tag{1}$$

Equation (2), in which $E_+$ is the ground state surface on which ET occurs. Both Marcus and Hush chose the diabatic surfaces as parabolas centered at 0 and 1 on an ET coordinate $X$ (the dashed surfaces in Figure 1).

$$E_\pm = 0.5\{(H_0 + H_1) \pm [(H_0 - H_1)^2 + 4H^2]^{1/2}\} \tag{2}$$

Symmetrical Class II compounds have their diabatic minima at the same energy and a vertical separation at $X = 0$ and 1 equal to Marcus's vertical reorganization energy, $\lambda$.[3] The electronic mixing $H$ causes the ground state adiabatic surface $E_+$ to be a double minimum well with a maximum at an energy of $\lambda/4 - H$ lying at $X = 0.5$, and with symmetrically disposed minima at energy $-H^2/\lambda$ lying near $X = 0$ and 1 when $H$ is small, but increasingly closer to 0.5 as $H$ increases. The thermal electron-transfer barrier $\Delta G^*$ is thus given by Equation (3).[3b] Although Hush's derivation used perturba-

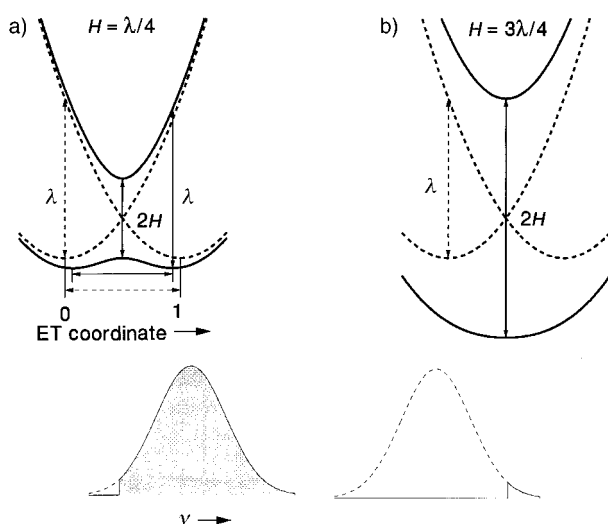$$\Delta G^* = (\lambda/4 - H) + H^2/\lambda \tag{3}$$

Figure 1. Energy plots (above) and resulting optical spectra illustrating the cutoff discussed in the text (below) using the Marcus–Hush classical two-state model for: a) a Class II intervalence compound, drawn for $H = \lambda/4$, and b) a Class III compound, drawn for $H = 3\lambda/4$. Parabolic diabatic energy surfaces are shown as the dashed lines at 0 and 1 on the ET coordinate; they are separated by $\lambda$ at the energy minima. The adiabatic surfaces calculated using Equation (2) are shown as solid lines. For a), $H < \lambda/2$, the band maximum ($\tilde{\nu}_{max}$) occurs at $\lambda$, but for b), $H > \lambda/2$, the band maximum occurs at $2H$.

tion theory, and it was sometimes thought that it should break down as $H$ increased, Creutz, Newton, and Sutin have pointed out that Equation (2) is the solution for Equation (1) at all values of $H$,[4] so Equation (3) is valid at all sizes of $H < \lambda/2$ in this model.

The barrier to ET disappears at $H = \lambda/2$, and the compound becomes a Class III, delocalized system for this and higher values of $H$ (see Figure 1b).

Hush pointed out that for this model,[2] when $H$ is large enough to observe it, there will be an intervalence charge transfer (IT) band with an optical transition energy at the band maximum, $\tilde{\nu}_{max} = \lambda$.[6] $\tilde{\nu}_{max}$ (also often called $E_{op}$ or $\hbar\omega_{max}$) is invariant with $H$ for Class II compounds, and $H$ can be experimentally evaluated from the $IT$ band by using Equation (4), in which $\Delta\tilde{\nu}_{1/2}$ is the band width at half height (for a

$$H_{Hush} \; (cm^{-1}) = (0.0206/d) \; (\tilde{\nu}_{max} \Delta\tilde{\nu}_{1/2} \varepsilon_{max})^{1/2} \qquad (4)$$

Gaussian-shaped band), $\varepsilon_{max}$ is the extinction coefficient at the band maximum, and $d$ (Å) is the electron-transfer distance. A modified version of Equation (4) applicable to any band shape is available[2] and is frequently used for bands that have non-Gaussian shape.[11–13, 15, 18b]

Equation (4) remains by far the most commonly used method of evaluating $H$ for Class II compounds. By using Marcus–Hush theory, the band shape for a Class II compound is the very broad, Gaussian shaped curve shown as the dashed bands at the bottom in Figure 1. The energy coordinate $\tilde{\nu}$ for the optical spectrum is given by the energy gap between the adiabatic surfaces (the solid lines in Figure 1), and the intensity coordinate by the increase in energy from the minimum on the ground state surface (see below). The key point that people had not considered is that $\tilde{\nu}$ cannot be less

than the smallest energy gap between the ground and excited states; this occurs at $X = 0.5$, and is $2H$ for both Class II and III systems (see Figure 1). It has long been known that anomalously narrow bands were observed near the borderline, but the classical origin of this narrowing and its implication for the use of Equation (4) (see below) had not been pointed out. Both transition metal and organic-centered examples of compounds near enough the borderline to show this $2H$ cutoff in their optical spectra have recently been published, as will be described below.

Creutz and Taube reported the synthesis and optical spectrum of the first symmetrical intervalence compound with transition metal centers, with $\mathbf{M = (NH_3)_5Ru}$, and $\mathbf{B = pyz}$, charge $= +5$.[7] It was first thought that this Creutz–Taube complex might be a Class II compound that lay near the II/III borderline, but extensive experimental and theoretical work by many groups have established that without doubt, it is Class III.[5] Several IT bands occur in the intervalence oxidation state of metal-centered compounds, but only the lowest energy one may be used with Equation (4) to estimate $\Delta G^*$. The absorption band originally assigned as a Class II IT band is actually the third absorption band of this delocalized compound. A vibronic coupling two-state model that considers band shape and position for all of the IT bands was introduced by Piepho and co-workers.[8] The lowest energy band for the Creutz–Taube complex occurs in the IR region and is so weak and broad that it was not observed until its position had been calculated.[5b] Not surprisingly, the bridge must also be included as a third state to properly describe all of the intervalence bands and the resonance Raman spectra.[9] Hush theory is far simpler than vibronic coupling theory and it does not allow the prediction of the positions of charge-transfer bands. It does produce $H$ in a simple manner when the proper band is observed. We have compared $H$ values estimated by using Equation (4) for Class II examples and $\tilde{\nu}_{max} = 2H$ for Class III examples of some metal-centered and organic intervalence compounds, finding good agreement with the changes in $H$ expected as $\mathbf{B}$ is enlarged.[10]

Creutz, Newton, and Sutin recently introduced a new optical method for extracting the $\mathbf{M}$-to-$\mathbf{M'}$ $H$ value that Hush obtained, by analyzing the often higher energy and easier to see $\mathbf{M}$-to-$\mathbf{L}$ ($\mathbf{L}$ stands for the bridging ligand) band. This "CNS" method retains the simplicity of Hush theory because it employs the analogue of Equation (4) to determine $H_{LM}$ for this band, and uses the expression $H_{MM'} = H^2_{LM}/\Delta E^{eff}_{LM}$, in which the denominator is a reduced energy term obtained from $\tilde{\nu}_{max}$ values for the two bands.[4] We will call the electronic interactions obtained in this manner $H_{CNS}$ values. Good agreement between $H_{Hush}$ and $H_{CNS}$ values were found when $d_{LM}$ was set equal to half of the $\mathbf{M-M'}$ distance.[4]

Interest remains strong in Class II intervalence compounds with transition metal centers that lie near the borderline and therefore have exceptionally fast thermal ET. We shall consider recent work in this area by the groups of Crutchley, Meyer, Geiger and Giese, Gourdon and Launay, and Ito and Kubiak.[11–15] It has also become evident that compounds with organic charge-bearing units fit into the Robin–Day, Hush intervalence compound framework. Cowan and co-workers

first applied the term in 1973 to an organic compound, pointing out that tetrathiafulvalene radical cation is a Class III compound.[16] The first organic radical cations ever made, *p*-phenylenediamine radical cation and its derivatives, are also Class III compounds. They are structural analogues of the Creutz–Taube complex, with two $NR_2M$ units (instead of $(NH_3)_5Ru$ units) linked through in-plane bonds (CN instead of RuN) to a six-membered aromatic ring. We will also discuss work on intervalence compounds that contain two tetrathia-fulvalene–**M** units,[17] and those with triarylamine units.[18]

**The two-state classical model near the II/III borderline**: Although intervalence compounds often have been said to be "near the II/III borderline", we have seen little discussion of how this is best defined. Most people have followed Hush in using the mixing coefficient $\alpha$, approximated as $H/\tilde{\nu}_{max}$. But $\alpha$ is $(X_{min})^{1/2}$ for the adiabatic ground state surface ($E_+$), which is given exactly by Equation (5).[3b] The $H/\tilde{\nu}_{max}$ approximation

$$X_{min} = 0.5\{1 - (1 - 4H^2/\tilde{\nu}_{max}^2)^{1/2}\} \quad (5)$$

becomes increasingly poor as the borderline is approached, and both $\alpha$ (which goes to 0.707) and $X_{min}$ (which goes to 0.5) are quite non-linear with the fraction of the ET barrier caused by vertical reorganization energy that remains after electronic interaction is included ($F$).

Equation (3) may be factored to produce Equation (6), so the expression for $F$ is simple. Considering where a measured

$$\Delta G^* = F(\tilde{\nu}_{max}/4) \qquad F = (1 - 2H/\tilde{\nu}_{max})^2 \quad (6)$$

$H$ value positions an intervalence system between its Class I and Class III limits depends greatly upon whether the adiabatic minima separation or the $\Delta G^*$ remaining is considered to be the criterion (see Figure 2). When $H = \tilde{\nu}_{max}/4$, half-way between the Class I and Class III limits, the
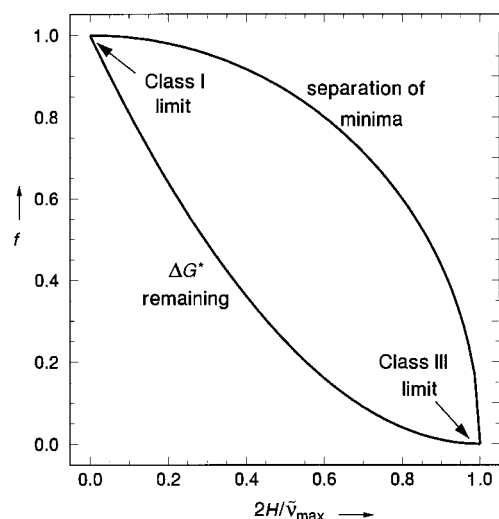


Figure 2. Comparison of the change in the separation of the adiabatic minima [$f = 1 - 2X_{min}$ of Eq. (5) is plotted] and in the barrier remaining for ET [$f = F$ of Eq. (6) is plotted] as $H$ is increased to move a Class II intervalence compound from its Class I to its Class III border, by using the two-state classical model.

adiabatic minimum separation has only dropped 13%, but $\Delta G^*$ has dropped 75%, and the slopes at the II/III borderline are very large and zero, respectively.

Because $F$ is linear with the barrier for ET, and we consider disappearance of $\Delta G^*$ to be the best definition of the II/III borderline, we will use $F$ in considering how near the II/III borderline various systems lie.

We recently pointed out explicitly that the band shape for IT bands in the two state classical model may be calculated by simply assuming a Boltzmann equilibrium on the ground state energy surface, that is, that the extinction coefficient at a given energy, $\varepsilon(\tilde{\nu})$, is given by Equation (7), and $\tilde{\nu}$ is the adiabatic energy difference between the excited state and ground state.[19]

$$\varepsilon_{rel} = \varepsilon(\tilde{\nu})/\varepsilon_{max} = \exp(-\Delta E/RT) \quad (7)$$
$$\Delta E = \{E(\tilde{\nu}) - E_{min}\} \quad (7a)$$

As shown in Figure 1, the most important fact for considering optical spectra near the borderline is that $\tilde{\nu}$ for an IT band can never be less than $2H$, the $\Delta E$ at $X = 0.5$. When $\Delta G^*$ is small, $\varepsilon_{rel}$ will still be substantial at $\tilde{\nu} = 2H$, changing the shape of the band. The two-tate classical model produces a Gaussian-shaped IT band that is symmetrical about $\tilde{\nu}_{max}$, and has a band width given by Equation (8), in which HTL stands for high-temperature limit (the full band shape is shown as the dashed lines in Figure 1).[2]

$$\Delta\tilde{\nu}_{1/2}(HTL) = (16 RT \ln(2)\tilde{\nu}_{max})^{1/2} \quad (8)$$

Band shape is invariant with $H$ for most $\tilde{\nu}$, but the band cuts off and $\varepsilon_{rel}$ plunges to zero when $\tilde{\nu}$ drops below $2H$.[20] As indicated in Figure 1, this cutoff does not become very significant until $H$ exceeds the $\lambda/4$ used in drawing Figure 1a. A discontinuity in the $\varepsilon_{rel}$ versus $\tilde{\nu}$ plot is evidently physically unreasonable. Quantum effects will "round off the corners", but band shape will clearly be affected when the $\varepsilon_{rel}$ cutoff occurs at a significant fraction of $\varepsilon_{max}$. The band is cut off at $\varepsilon_{max}/n$ when $\Delta G^*$ becomes $RT\ln(n)$, which leads to a simple equation for the $H$ value at cutoff, $H_{cut}(n)$ [Eq. (9)].

$$H_{cut}(n) = (\tilde{\nu}_{max}/2)(1 - 2[RT\ln(n)/\tilde{\nu}_{max}]^{1/2}) \quad (9)$$

Figure 3 shows a plot of $\Delta\tilde{\nu}_{1/2}$ versus $H/\tilde{\nu}_{max}$ for the two-state classical model. Once $H_{cut}(2)$ is exceeded, band width decreases linearly as $2H$ occurs at a higher fraction of $\varepsilon_{max}$ until the borderline is reached. This band truncation makes the area under the curve 88% of that for a small $H$ compound when cutoff occurs at $0.5\varepsilon_{max}$, 78% at $0.75\varepsilon_{max}$, and 50% at the II/III borderline, at which the band has been sliced in half. If Equation (4) or its modification for non-Gaussian band shape is used,[11–13, 15, 18] $H$ will be increasingly underestimated as the system approaches the borderline, and the under-estimation should reach 50% near the II/III borderline (considering only the cutoff effect). As $H$ increases further, in the Class III region, the band continues to narrow because curvature at the $E_+$ minimum increases. The narrowing will sharply increase $\varepsilon_{max}$ as $H$ increases relative to $\tilde{\nu}_{max}$, and
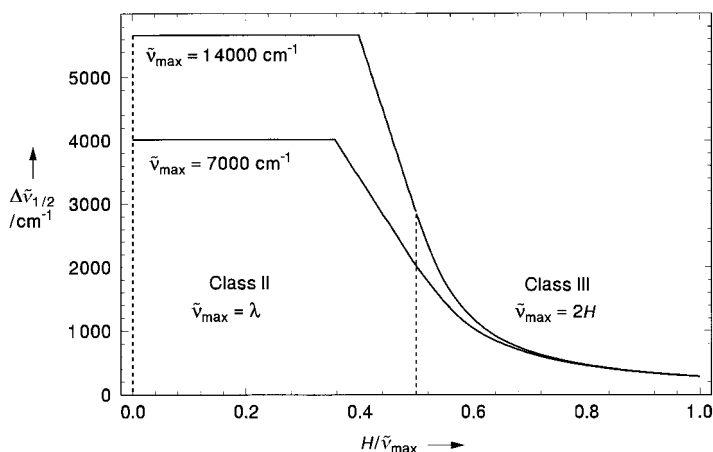
Figure 3. Two-state classical model line width at half height as a function of $H/\tilde{\nu}_{max}$.

Table 1. IT band width ratio and $F$ values for **dicyd** derivatives.[a]

| M | B | Solvent | R[b] | $H_{CV}$ [cm$^{-1}$] | $H_{CNS}$ [cm$^{-1}$] | $F_{CV}$ | $F_{CNS}$ |
|---|---|---|---|---|---|---|---|
| **(NH$_3$)$_5$Ru** | **Me$_2$H$_2$**[c] | MeCN | 0.60 | 2930 | 2190 | 0.030 | 0.146 |
| | | Me$_2$CO | 0.59 | 2700 | 1630 | 0.049 | 0.280 |
| | | Me$_2$SO | 0.90 | 2030 | 870 | 0.168 | 0.569 |
| | **H$_4$** | MeNO$_2$ | 0.61 | 2780 | 1980 | 0.036 | 0.181 |
| | | MeCN | 0.69 | 2610 | 1680 | 0.058 | 0.269 |
| | | Me$_2$CO | 0.70 | 2190 | 1230 | 0.123 | 0.404 |
| | | Me$_2$SO | 1.02 | 1880 | 780 | 0.249 | 0.627 |
| | **Cl$_2$H$_2$** | MeCN | 0.85 | 2120 | 1090 | 0.149 | 0.469 |
| | | Me$_2$CO | 0.94 | 1820 | 900 | 0.235 | 0.556 |
| | | Me$_2$SO | 1.35 | 1570 | 550 | 0.366 | 0.742 |
| | **Cl$_4$** | MeCN | 0.95 | 1620 | 710 | 0.310 | 0.650 |
| **(NH$_3$)$_4$pyrRu** | **Me$_2$H$_2$**[c] | MeCN | 0.46 | 3290 | 3360 | 0.104 | 0.010 |
| | | Me$_2$SO | 0.61 | 2530 | 1270 | 0.059 | 0.374 |
| | **H$_4$**[c] | MeCN | 0.51 | 3065 | 3070 | 0.023 | 0.023 |
| | | Me$_2$SO | 0.73 | 2200 | 1580 | 0.101 | 0.261 |
| | **Cl$_2$H$_2$** | MeCN | 0.69 | 2370 | 1840 | 0.084 | 0.202 |
| | | Me$_2$SO | 0.94 | 2660 | 980 | 0.269 | 0.513 |
| | **Cl$_4$** | MeCN | 0.86 | 1920 | 1370 | 0.173 | 0.362 |
| | | Me$_2$SO | 1.08 | 1490 | 710 | 0.373 | 0.664 |
| **(NH$_3$)$_3$bpyRu** | **Cl$_2$H$_2$** | MeCN | 0.61 | 2830 | 3010 | 0.349 | 0.017 |
| | | Me$_2$SO | 0.90 | 2040 | 1640 | 0.465 | 0.238 |

[a] Calculated from the data of ref. [9]. [b] R $= \Delta\tilde{\nu}_{1/2}$(obsd)/$\Delta\tilde{\nu}_{1/2}$(HTL).
[c] IR studies in acetonitrile indicate that the **M = (NH$_3$)$_4$pyrRu**, **B = Me$_2$H$_2$** compound, which has the smallest $F_{CV}$, is delocalized on the IR timescale, and is therefore now assigned as Class III, but evidence for localization on the IR timescale is found for both the **M = (NH$_3$)$_4$pyrRu**, **B = H$_4$** compound and the **M = (NH$_3$)$_5$Ru**, **B = Me$_2$H$_2$** one.[11b]

vibrational fine structure on the high energy side will be come visible if the excited state geometry resembles that of the ground state, so that the transition remains vertical. The optical spectrum is not expected to strongly signal the crossing of the II/III borderline, as a cutoff Class II spectrum will greatly resemble a Class III spectrum for which there is still so much broadening that vibrational structure is not resolved.

**Transition metal centered intervalence compounds**: Crutchley and co-workers have obtained the most extensive data set for related compounds lying near the borderline, for diruthenium-1,4-dicyanamidobenzenes (**dicyd** derivatives, Scheme 1).[11] We will only consider systems for which they were able to get data allowing estimation of $H$ by three different methods. These are **B = dicyd** (we abbreviate it **H$_4$**), and three derivatives: 2,5-dimethyl- (**Me$_2$H$_2$**), 2,5-dichloro- (**Cl$_2$H$_2$**) and tetrachloro-substituted (**Cl$_4$**) **dicyd**. The **M** groups include **(NH$_3$)$_5$Ru**, **(NH$_3$)$_4$pyrRu**, and **(NH$_3$)$_3$bpyRu**. The compound–solvent combinations for which complete data have been published[11] appear in Table 1. It will be noted from the $R = \Delta\tilde{\nu}_{1/2}$(obsd)/$\Delta\tilde{\nu}_{1/2}$(HTL) column that most of the observed band widths are significantly smaller than the $\Delta\tilde{\nu}_{1/2}$(htl) values obtained from Equation (8). As pointed out above, this is an indication of approaching (or passing) the II/III borderline. They tabulate $H_{Hush}$ and $H_{CNS}$ values. These optical methods of estimating $H$ were compared with the thermodynamic estimate of electronic coupling obtained from the difference in formal potentials, $\Delta E°$, for ET on each side of the intervalence oxidation state (determined by cyclic voltammetry), and the singlet, triplet gap for the diradical oxidation state.[11] The parameter thus obtained, $\Delta G_r'$, was equated to $H^2/\tilde{\nu}_{max}$ (the stabilization of the adiabatic energy minimum compared with the diabatic minimum) and the energy minimum stabilizations estimated by the three methods were compared. It was decided that $H_{CNS}$ gave reasonable predictions throughout the range of coupling studied because $H_{CNS}^2/\tilde{\nu}_{max}$ correlates reasonably with $\Delta G_r'$. The size of the electronic coupling estimated by the thermodynamic method [we shall call it $H_{CV} = (\tilde{\nu}_{max}\Delta G_r')^{1/2}$] was not compared with $H_{CNS}$,[11] but is in Table 1. The $H_{Hush}$ values for these **dicyd** derivatives vary little with either bridge or solvent, very different behavior than

either $H_{CV}$ or $H_{CNS}$, and it was concluded that $H_{Hush}$ is not close to the true $H$.[11] Plots of the fraction of the predicted band width for the IT band, $\Delta\tilde{\nu}_{1/2}$(obsd)/$\Delta\tilde{\nu}_{1/2}$(HTL) [Table 1, column 4], versus $F_{CV}$ and $F_{CNS}$ appear as Figures 4a and 4b respectively. For $\tilde{\nu}_{max} = 7000$ cm$^{-1}$ (a typical value for these compounds), cutoff at $\varepsilon_{max}/2$ occurs at $H = 2498$ cm$^{-1}$ ($F = 0.082$), and at $\varepsilon_{max}/4$ at $H = 2082$ cm$^{-1}$ ($F = 0.164$); this will noticeably alter band shape. There is a clear trend for the band width ratio decreasing rather sharply and in about the expected range for the plot versus $F_{CV}$, while the plot versus $F_{CNS}$ shows decrease at too high $F$, and does not drop reasonably with further decrease in $F_{CNS}$. We suggest that this is experimental evidence for $H_{CV}$ being a more reliable estimate of the true $H$ for these **dicyd**-bridged compounds, as was assumed by Crutchley and co-workers. The difference between $H_{CNS}$ and $H_{Hush}$ is very dependent on compound and solvent. A plot of this difference versus $F_{CV}$ reveals that $(H_{CNS} - H_{Hush})$ increases markedly as $F_{CV}$ decreases to values for which the cutoff appears in the region the absorbance data were recorded (see Figure 5). We believe this analysis makes it clear that Equation (4) gives values of $H$ that are too small when $\varepsilon_{rel}$ at the cutoff is significant, and also that $H_{Hush}$ and $H_{CNS}$ give within experimental error of the same number for these compounds when the cutoff is not significant, as demonstrated earlier for other compounds that were not near the cutoff.[4] There is still a discrepancy approaching a factor of two between $H_{CV}$ and optically derived $H$ when the cutoff is not a problem. A contributing factor may be the use of too large a $d$ value in obtaining $H$ values from the optical data.[21–24] A recent study indicates that the smallest $F_{CV}$ system of Table 1 is delocalized on the IR timescale (Table 1, footnote c),[11b] but that most of the others are probably
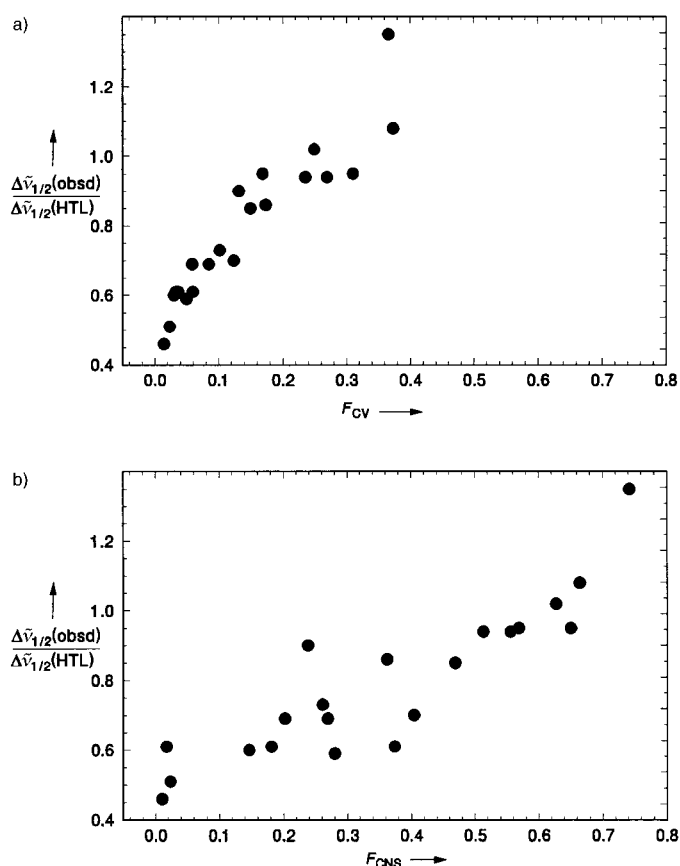
Figure 4. Plots of the ratio of observed IT band width to that calculated by Equation (8) versus a) $F_{CV}$ and b) $F_{CNS}$ for the Crutchley et al. **dicyd** derivatives[11] (Table 1).
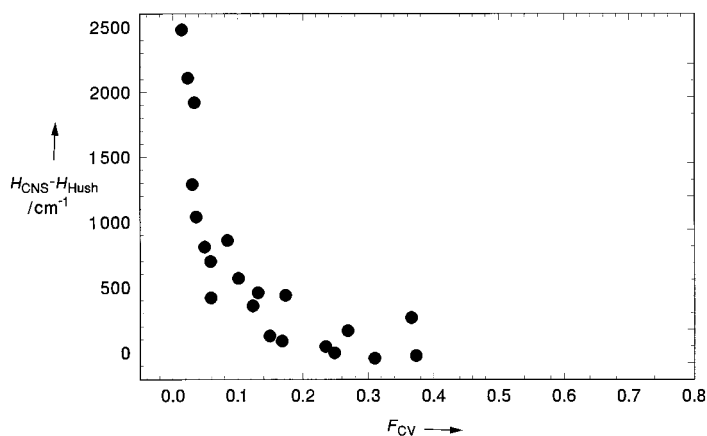


Figure 5. Plot of the difference between $H_{CNS}$ and $H_{Hush}$ versus $F_{CV}$ for the data of Table 1.

localized, as has been assumed when Equation (4) is employed.

Meyer and co-workers have shown that the Creutz–Taube complex analogue **M = bpy₂ClOs**, **B = pyz**, lies very near the II/III borderline.[12a] It has an anomalously narrow IT band that is partially buried under another band and was obtained by deconvolution. Its IR spectrum in the pyrazine stretch region indicates instantaneously localized charge, but rapid ET on the IR timescale. Analysis of the IT band by using the non-Gaussian modification of Equation (4) gave $\tilde{v}_{max} =$

2620 cm⁻¹, $H_{Hush} = 247$ cm⁻¹.[12a] These values correspond to $F_{Hush} = 0.65$, which is larger than is consistent with the tiny barrier required for ET being fast on the IR timescale, or the distortion of the IT band observed. Once again, the $H_{Hush}$ obtained by using Equation (4) analogues proves to be unreasonably low, presumably at least partially because of the cutoff. $H$ would need to approach about four times the $H_{Hush}$ value quoted to be consistent with the low barrier indicated by the IR spectrum. In addition to the cutoff effect, perhaps the $d$ used (the metal–metal distance, as is customary[2]) is inappropriately large. In even more recent work, Meyer and co-workers have studied four examples of Os^II,Os^III-centered intervalence complexes with **B = N₂** that lie near the borderline. They have **M =** *cis,cis* **bpy₂ClOs**, *trans,trans* **bpy₂ClOs**, **tpmCl₂Os**, and **TpCl₂Os**, where **tpm =** tris(1-pyrazoyl)methane and **Tp =** tris(1-pyrazoyl)borate (see Scheme 1).[12b] All show N₂ stretches in the IR spectra, showing that their metal substituents are different, and five bands associated with the metal d orbitals and the N₂ bridge. The two lowest energy IT bands are assigned as metal dπ→dπ. $H$ values for the IT bands are extracted by using the Hush equation and the metal, metal distance as $d$. The $H$ values for the three bands assigned as metal-to-metal ones are summed, although the relationship between this sum and the shape of the lower energy surface is not discussed.[12b] Significant band truncation effects appear to be present for all the bands observed; this making use of the Hush equation for calculating $H$ inaccurate. These systems probably would need at least a three-state analysis for accurate determination of $\Delta G^*$ because both the dπ→dπ bands are low in energy.
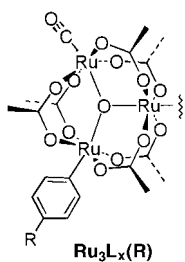
Gourdon and Launay report an optical analysis of **M = tpyRu**, **B = tphz** (5 +) (see Scheme 1).[13] Despite the same number of bonds in the bridge as the Creutz–Taube complex, and the corresponding **B = tpp** complex being delocalized, this compound was assigned as Class II from its optical spectrum. They report $\tilde{v}_{max} = 7400$ cm⁻¹ and $H = 403$ cm⁻¹ using Equation (4). These numbers give an $F$ value of 0.79, which corresponds to strong trapping. They point out special geometrical reasons for the rather large $\Delta E°$ of 3550 cm⁻¹ at such a small $H$ for their compound, with which we agree qualitatively. They do not point out that the $\Delta\tilde{v}_{1/2}$ reported is only 54% of the value derived from Equation (8), which would not occur if there were such strong trapping. We suggest that once again, analysis of a compound near the borderline by means of Equation (4) and what may be an unreasonably large $d$ value (6.86 Å, not quoted in the paper, was employed) has led to serious underestimation of $H$.

Geiger and Gleiter have shown that the σ-bond-bridged system $[(L_nCo)_2]^+$ is localized on the IR timescale.[14] Most of their discussion concerns matters that Hush theory does not address, and we shall only consider one point here. Although non-intervalence model compounds predict $\Delta\tilde{v}_{CO}$ of 26 cm⁻¹ between the CO₂Me groups on rings coordinated to the 0 and 1 + charged Co units, the value observed is 21 cm⁻¹, and the difference is attributed



(LnCo)₂
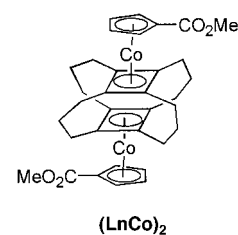
to charge transfer associated with mixing of the wave functions by a large $H$ value.[13] The ratio 21/26 indicates formal charges of 0.19 and 0.81 at the metals (instead of the 0 and 1 that are the $H \rightarrow 0$ limits), which we point out is equivalent to $X_{min}$ for the adiabatic surface having these values. In the two-state model, these $X_{min}$ values occur for $F = 0.04$, and at the observed $\tilde{v}_{max} = 6500$ cm$^{-1}$, this corresponds to $H = 2600$ cm$^{-1}$. Large mixing is also qualitatively consistent with the observed IT band width at half-height being only 68% of the value derived from Equation (8).[14]
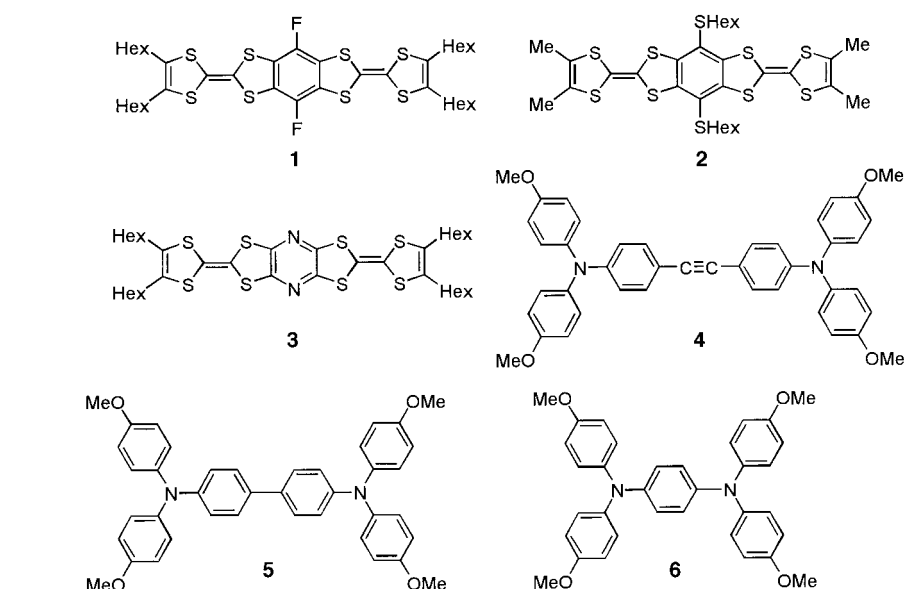


Scheme 2. Neutral precursors of organic intervalenece compounds.

Ito, Kubiak, and co-workers showed that two examples of the Cruetz – Taube complex analogue **M = Ru₃Lₓ(R)**, **B = pyz** are also very near the II/III borderline, with broadened IR spectra in the CO stretch region because of rapid ET.[15a] The **R = CN**, **B = pyz** example has $\tilde{v}_{max} = 10\,700$ cm$^{-1}$, $H_{Hush} = 1300$ cm$^{-1}$ ($F = 0.58$), a calculated ET rate constant of $1 \times 10^9$ s$^{-1}$, and shows separate, partially overlapping CO stretch bands (leading to a rate constant estimate[15b] of $\sim 1 \times 10^{11}$ s$^{-1}$). The **R = H** and NMe₂ examples exhibit clear IR band broadening, and rate constants derived from the IR spectrum are $5 \pm 3 \times 10^{11}$ and $9 \pm 3 \times 10^{11}$ s$^{-1}$, respectively.[15] We note that the $F$ values for them, calculated from the reported $\tilde{v}_{max}$ and $H_{Hush}$ values, are both 0.42, and the calculated ET rate constants $5.4 \times 10^9$ and $5.7 \times 10^9$, respectively. So once again, Equation (4) produced $H_{Hush}$ values that are too low for compounds near the II/III borderline.[25] More recently, the **B = 4,4'-bpy** analogues, which have smaller $H$ and far slower ET have also been studied,[15b] but they are not near the II/III borderline.

**Organic-centered intervalence compounds**: Among several examples that could have been selected, we discuss the intervalence (+1) oxidation states of the largely sulfur- and nitrogen-centered compounds shown in Scheme 2.

Both tetrathiafulvalene (TTF) and triarylamines have small internal reorganization energies upon electron loss, so that like intervalence compounds with transition metal centers, they should have $\tilde{v}_{max}$ values that approach the solvent component of $\lambda$. The **M = TTF** analogues **1 – 3** are doubly attached to the same 6-membered aryl ring, have three bonds connecting the sulfur atom "edges" of the charge-bearing units, and might be expected to show large $H$ values, which would place them in the region of interest here. The optical spectrum analysis reported[17] is summarized in Table 2. It is seen from the $F_{Hush}$ column that none of the TTF-based compounds have small enough $F$ to expect cutoff effects. We suggest that this is incorrect for **3⁺**, for which the data are

Table 2. Optical parameters for some organic-centered intervalence compounds in CH₂Cl₂.

| | $\tilde{v}_{max}$ [cm$^{-1}$] | $H_{Hush}$ [cm$^{-1}$] | $F_{hush}$[a] | $\Delta G^{*[b]}$ [cm$^{-1}$] |
|---|---|---|---|---|
| **1⁺[c]** | 6000 | 1000 | 0.52 | 750 |
| **2⁺[c]** | 5750 | 800 | 0.44 | 670 |
| **3⁺[c,d]** | *4000* | *785* | *0.37* | *370* |
| **4⁺[e]** | 6190 | 1200 | 0.65 | 580 |
| **5⁺[e]** | 6360 | 1550 | 0.57 | 420 |
| **6⁺[e]** | 9530 | 3240 | 0.12 | 240 |

[a] Calculated by using Equation (6). [b] Calculated by using Equation (3). [c] Data from ref. [17]. [d] Shown in italics because this compound is argued to be localized (see text). [e] Data from ref. [18b].

shown in italics, because we believe that there is a problem with them. The IT band for **3⁺** is much narrower than that for **1⁺** and **2⁺**, but has $\varepsilon_{max}$ a factor of three higher and $\tilde{v}_{max}$ only 2/3 as large, making $H_{Hush}$ only slightly smaller. But the IT band shape for **3⁺** (Figure 6)[26] is completely different than that for **1⁺** and **2⁺**,[17] which resemble the Gaussian curves expected for Class II compounds. Figure 6 does not look to us much like a cutoff Class II IT band (which would remain a half-Gaussian on the high-energy side of the maximum), but resembles that expected for a Class III compound that has a nearly vertical transition with a rather large vibrational progression, but considerable line width. We suggest that **3⁺** is a Class III, delocalized compound, in which case the $\tilde{v}_{max}$ value gives $H = 2000$ cm$^{-1}$. This assignment requires that changing from the benzene rings of **1⁺** and **2⁺** to the pyrazine ring of **3⁺** greatly increases $H$. We presume that this occurs because both the bridge HOMO and LUMO are greatly stabilized by changing two atoms of the π system from carbons to nitrogen. This can substantially increase $H$ because its value is controlled by
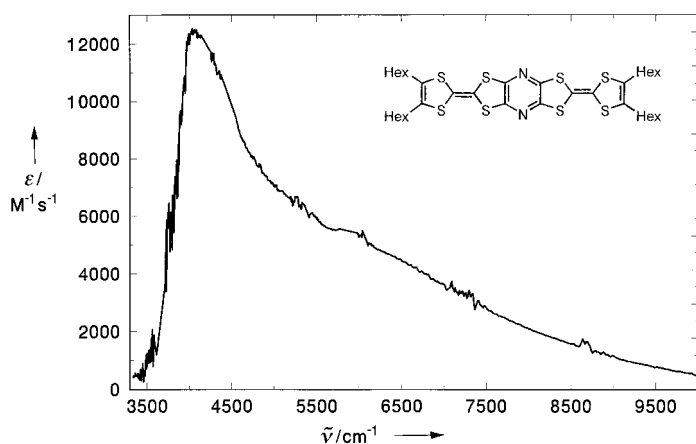
Figure 6. Plot of $\varepsilon$ versus $\tilde{\nu}$ for the *IT* band of **3**[+].

superexchange interactions that depend upon energy gaps as well as distance.[4, 27]

*H* increases as the bridge length is decreased in the triarylamine-centered compounds **4**[+]–**6**[+].[18b] Despite uncertainty in what to use for *d* (Lambert and Nöll used the N–N distance calculated by AM1), it is clear that cutoff effects are both expected and seen for **6**[+], for which the high energy to low energy half width ratio is 1.76.[18b]

## Conclusion

Application of Hush's equation [Eq. (4)] and its analogues for analysis of IT bands for compounds that are near the II/III borderline produces $H_{Hush}$ estimates that are too low because the experimental band is truncated at $\tilde{\nu} = 2H$ (and possibly for other reasons). For Crutchley's **bicyd** derivatives, $H_{Hush}$ and the $H_{CNS}$ calculated by using the bridging-ligand–metal CT band are numerically close when truncation problems for the band used in obtaining $H_{Hush}$ are absent and the ET distances used differ by a factor of 2. An organic-centered compound (**6**[+]) close enough to the II/III borderline to show the effect of the charge-transfer band cutoff is now available in Lambert and Nöll's work. It is argued from its band shape that the **TTF**-centered compound **3**[+] has passed the borderline, and is Class III (delocalized).

## Acknowledgments

[1] M. B. Robin, P. Day, *Adv. Inorg. Radiochem.* **1967**, *10*, 247.
[2] a) N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 391–444; b) N. S. Hush, *Electrochim. Acta* **1968**, *13*, 1005–1023; N. S. Hush, *Coord. Chem. Rev.* **1985**, *64*, 135–157.
[3] For reviews of Marcus theory see: a) R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265–322; b) N. Sutin, *Prog. Inorg. Chem.* **1983**, *30*, 441–99;

[4] C. Creutz, M. D. Newton, N. Sutin, *Photochem. Photobiol. A* **1994**, *82*, 47.
[5] a) C. Creutz, *Prog. Inorg. Chem.* **1983**, *30*, 1–73; b) R. J. Crutchley, *Prog. Inorg. Chem.* **1994**, *41*, 273–325.
[6] We will call $\lambda$ values evaluated from the IT band transition energy $\tilde{\nu}_{max}$, to distinguish them from other estimates of $\lambda$. For example, if vibronic coupling theory is used for analysis of the CT band, $\lambda$ is always slightly larger than $\tilde{\nu}_{max}$.
[7] C. Creutz, H. Taube, *J. Am. Chem. Soc.* **1969**, *91*, 3988.
[8] S. B. Piepho, E. R. Krausz, P. N. Schatz, *J. Am. Chem. Soc.* **1978**, *100*, 2996.
[9] a) V. Petrov, J. T. Hupp, C. Mottley, L. C. Mann, *J. Am. Chem. Soc.* **1994**, *116*, 2171; b) H. Lu, V. Petrov, J. T. Hupp, *Chem. Phys. Lett.* **1995**, *235*, 521 (and references therein).
[10] S. F. Nelsen, H. Q. Tran, *J. Am. Chem. Soc.* **1998**, *120*, 298.
[11] a) C. E. G. Evans, M. L. Naklicki, A. R. Rezvani, C. A. White, V. V. Kondratiev, R. J. Crutchley, *J. Am. Chem. Soc.* **1998**, *120*, 13096; b) M. C. DeRosa, C. A. White, C. E. B. Evans, R. J. Crutchley, *Inorg. Chem.*, submitted.
[12] a) K. D. Demadis, G. A. Neyhart, E. M. Kober, T. J. Meyer, *J. Am. Chem. Soc.* **1998**, *120*, 7121; b) K. D. Demadis, E.-S. El-Samanody, G. M. Coia, T. J. Meyer, *J. Am. Chem. Soc.* **1999**, *121*, 535.
[13] A. Gourdon, J.-P. Launay, *Inorg. Chem.* **1998**, *37*, 5336.
[14] M. E. Stoll, S. R. Lovelace, W. F. Geiger, H. Schimanke, I. Hyla-Kryspin, R. Gleiter, *J. Am. Chem. Soc.* **1999**, *121*, 9343.
[15] a) T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, J. Washington, C. P. Kubiak, *Science* **1997**, *277* 660; b) T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, H. Kido, I. S. Zavarine, T. Richmond, J. Washington, C. P. Kubiak, *J. Am. Chem. Soc.* **1999**, *121*, 4625.
[16] D. O. Cowan, C. LeVanda, J. Park, F. Kaufman, *Acc. Chem. Res.* **1973**, *6*, 1.
[17] K. Lahlil, A. Moradpour, C. Bowlas, F. Nenou, P. Cassoux, J. Bonvoisin, J. P. Launay, G. Dive, D. Dahareng, *J. Am. Chem. Soc.* **1995**, *117*, 9995.
[18] a) C. Lambert, G. Nöll, *Angew. Chem.* **1998**, *110*, 2239; *Angew. Chem. Int. Ed.* **1998**, *37*, 2107; b) C. Lambert, G. Nöll, *J. Am. Chem. Soc.* **1999**, *121*, 8434.
[19] S. F. Nelsen, R. F. Ismagilov, D. A. Trieber II, *Science* **1997**, *278*, 846.
[20] Lambert and Nöll include both the *F* expression and the cutoff in ref. [18].
[21] a) The *d* used in Equation (4) for **dicyd** derivatives was the X-ray metal–metal distance for an example (13.1 Å) $= 2d_{CNS}$.[4, 9] Hush theory uses *d* as the charge centers distance on the diabatic energy surfaces, which does not change with *H*, and estimates of the metal–metal distance are universally employed.[2] However, for strongly trapped (high *F*) methylated *p*-phenylene-bridged Class II bis(hydrazine) radical cations, slightly better fit to experimental rate constants is obtained using optical parameters derived by using an experimental estimate of *d* on the adiabatic energy surface, which of course does change with *H*.[22] Resonance Raman measurements provide an independent measure of *d* (we shall call it $d_{eff}$) on the adiabatic energy surface, and the values obtained can be significantly less than the metal–metal distance.[23] For example, Boxer's study of the IT band of **M = (NH$_3$)$_5$Ru, B = 4,4'-bpy** (5+) gave $d_{eff}$ of 52%/$f'$ of the metal–metal distance, ($f'$ is a correction believed to be close to unity).[23] This compound has $H_{Hush}$ and $E_{op}$ corresponding to $F = 0.85$,[24] so it is not near the II/III borderline. b) Evidently, however, the distance on the adiabatic surface, which goes to zero as the borderline is approached, cannot be used at the borderline. The effective distance for the **dicyd** derivatives may be smaller than 13.1 Å. For the higher $F_{CV}$ data sets, in which $H_{Hush}$ and $H_{CV}$ are within experimental error of each other (Figure 5), $H_{CNS}/H_{CV}$ averages 0.5 (range 0.35 to 0.72; there is a lot of scatter), and the use of $d_{eff} = 6.5$ Å as the **M,M'** distance in Equation (4) would improve agreement. For the 12 smaller $F_{CV}$ data sets, in which $H_{Hush}/H_{CNS}$ clearly decreases as $F_{CV}$ gets smaller, there is even more scatter, but $H_{CNS}/H_{CV}$ rises (average 0.8, range 0.56–1.06), so the effective *d* would have to increase as *F* decreases if allowing *d* to vary is to improve fit.
[22] a) S. F. Nelsen, R. F. Ismagilov, D. R. Powell, *J. Am. Chem. Soc.* **1997**, *119*, 10213; b) Diabatic surfaces deviating slightly from pure parabolas improve the fit to both the optical bands and the thermal barrier heights for strongly trapped bis(hydrazines),[19, 22a] but the changes in

band shape are quite small compared to cutoff effects near the II/III borderline that are discussed here.

[23] a) D. H. Oh, S. G. Boxer, *J. Am. Chem. Soc.* **1990**, *112*, 8061; b) G. U. Bublitz, S. G. Boxer, *Annu. Rev. Phys. Chem.* **1997**, *48*, 213; c) L. Karki, H. P. Lu, J. T. Hupp, *J. Phys. Chem.* **1996**, *100*, 15637.

[24] J. E. Sutton, H. Taube, *Inorg. Chem.* **1981**, *20*, 3125.

[25] In addition to problems from truncated area under the band because of the cutoff and possible problems with the effective *d*, we have some concern about the assignment of these bands as transitions from metal-to-metal across the pyrazine ring. This assignment requires that *H* more than doubles upon replacing the **M = (NH₃)₅Ru** of the Creutz – Taube compex by **M = Ru₃Lₙ(R)**. The charges are different, but increased delocalization in the **Ru₃** ligand should tend to substantially lower *H*. There may be a problem with intra-**Ru₃** bands occuring in the same region as the IT band. This would make these compounds (at least) three-state systems, to which the two-state Hush model would not apply quantitatively.

[26] Figure 6 plots the optical data for **3**⁺ versus energy instead of wavelength, as it was previously shown.[17]

[27] M. D. Newton, *Chem. Rev.* **1991**, *91*, 767 – 792.