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Molecular Structure Determination of Transient Species from Vibrational Frequency Data. Application to the ^{3}MLCT State of Tris(bipyridine)ruthenium(II)

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Abstract: A method is described whereby the results of normal-coordinate calculations are used to extract quantitative structural information for transient species from observed vibrational frequencies. The frequencies of the transient are compared to those of a precursor or those of a reference compound of known structure. The potential energy distributions (PED's), which specify the normal-mode compositions of the two species, are then used to convert the frequency shifts to bond length changes through a procedure that is based on a previously discovered empirical relationship between frequency and bond length. This procedure is employed to calculate the ^{3}MLCT-state structure of tris(bipyridine)ruthenium(II) with the results of previously reported normal-coordinate calculations for both the ground and ^{3}MLCT states. The effect of rotation of the normal modes in the excited state on the calculated structural parameters is briefly discussed.

The acquisiton of precise structural information for transient species, such as excited states and reaction intermediates, is of obvious importance for a detailed understanding of chemical and photochemical reaction pathways. In principle, such information is contained in vibrational frequency data. Thus, various well-known relationships between bond distances and vibrational frequencies (or stretching force constants) have been established, the most familiar being those proposed by Badger[1] and by Herschbach and Laurie.[2] Recently, Bürgi and Dunitz have provided a concise discussion of the physical basis for such empirical relationships.[3]

Such correlations are remarkably well-behaved for a wide range of diatomic molecules, providing an unambiguous relationship between bond length and vibrational spectroscopic data (frequency or force constant). However, in the case of polyatomic molecules, difficulty naturally arises inasmuch as the observed frequency, generally, is not associated with a particular bond but instead corresponds to a complicated motion involving many bonds. In order to relate vibrational frequency data to bond length changes, it is necessary, therefore, to obtain reliable estimates of normal-mode formulations. Thus, the availability of high-quality spectral data and reliable normal coordinates for two closely related systems may permit relatively precise determination of structural differences.

The considerable utility of such relationships is most effectively demonstrated by application to structural characterization of especially elusive species, such as electronically excited states. In fact, Woodruff, Meyer, and co-workers[4] have pointed out that such information is potentially available for the triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state of bis(bipyridine)ruthenium(II) and related complexes inasmuch as the ^{3}MLCT-state frequencies are directly available from time-resolved resonance Raman (TR^3) experiments.[5] However, as those authors emphasize, in the absence of reliable normal-mode descriptions, only average bond length changes can be deduced.

We recently completed comprehensive normal-mode calculations for both the ground and ^{3}MLCT excited states having employed 12 isotopomeric complexes.[6,7] As is shown here, these calculations, along with the ground- and ^{3}MLCT-state vibrational frequencies, provide the basis for a determination of individual bond length changes that accompany ^{3}MLCT-state formation.

Methods

Empirical Relations for Diatomic Molecules. The familiar "Badger's rule" relationship[1] between the equilibrium bond length (r_e) and stretching force constant is given in eq 1, where r_e is given in angstroms.

$$F = 1.86 \times 10^5 (r_e - d_{ij})^{-3} \qquad (1)$$

F is in units of dynes per centimeters, and d_{ij} is an empirical parameter that depends on the position of the bonded atoms in the periodic table. A somewhat simpler relationship (eq 2), discovered by Herschbach and Laurie,[2] gave a better fit to a larger set of data, where a_{ij} and b_{ij} are empirical constants that depend only on the rows of the periodic table to which the bonded atoms belong (i.e., for bonds between two first-row elements, $a_{11} = 1.73$ and $b_{11} = 0.47$). Later, Johnston[8] included data for other molecules and suggested other values of a_{11} (1.46) and b_{11} (0.55).

$$r_e = (a_{ij} - b_{ij}) \log F \qquad (2)$$

Such relationships are expected to be most reliable when used to determine bond length differences in closely related systems where there are no fundamental differences in the nature of the bonding. Thus, application of eq 2 to two similar systems yields eq 3. This can be

$$\Delta r = r_2 - r_1 = b_{ij} \log (F_1/F_2) \qquad (3)$$

reformulated in terms of vibrational frequencies

$$\Delta r = r_2 - r_1 = 2b_{ij} \log (\nu_1/\nu_2) \qquad (4)$$

To remain consistent with recent trends,[3,4] we express this relationship using natural logarithms and $b_{ij} = 0.47$ (eq 5). The equation in this form

$$\Delta r = r_2 - r_1 = 0.408 \ln (\nu_1/\nu_2) \qquad (5)$$

has been applied by Woodruff, Meyer, and co-workers to deduce average bond length changes (Δr) upon formation of the ^{3}MLCT state of Ru(bpy)$_3^{2+}$. Thus, they calculate $\Delta r \approx 0.01$ Å using various pairs of ground- and ^{3}MLCT-state frequencies.[4] As they point out, no further definition of bond length changes could be obtained in the absence of reliable normal-mode formulations. It should also be noted that Van Duyne and co-workers[9] have attempted to apply similar concepts to determine structural changes (relative to the neutral molecule) associated with the formation of organic anion radicals but also were hampered by the lack of reliable normal-mode descriptions.

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Extension to Polyatomic Systems. In order to successfully apply eq 5 to determine individual bond length changes, the essential task is to derive a method whereby the normal-mode descriptions can be exploited to relate observed frequency shifts to bond length changes. Careful consideration of the information derived from normal-coordinate calculations suggests such a method.

The total potential energy (V) for a given molecule may be expressed in terms of internal coordinates

$$2V = \sum_{i,j}^{3N-6} F_{ij} R_i R_j \qquad (6)$$

where F_{ij} and R_i and R_j are the force constants and internal coordinates, respectively. In turn, the internal coordinates are related to the normal coordinates in the fashion

$$R_i = \sum_{k=1}^{3N-6} L_{ik} Q_k \qquad (7)$$

where the L_{ik} are the components of the so-called L matrix. Thus, eq 6 and 7 may be combined to give an alternate expression for potential energy

$$2V = \sum_{i,j}^{3N-6} F_{ij} \sum_{k}^{3N-6} L_{ik} Q_k \sum_{k}^{3N-6} L_{jk} Q_k \qquad (8)$$

For a single mode, eq 8 simplifies to

$$2V(Q_k) = \sum_{i,j}^{3N-6} F_{ij} L_{ik} L_{jk} Q_k^2 \qquad (9)$$

or equivalently

$$2V(Q_k) = \lambda_k Q_k^2 \qquad (10)$$

where $\lambda_k = 4\pi^2\nu_k^2$. Equating expressions 9 and 10, it is seen that

$$1 = \sum_{i,j}^{3N-6} F_{ij} L_{ik} L_{jk} / \lambda_k \qquad (11)$$

which may be approximated as

$$1 \sim \sum_{j} F_{jj} L_{jk}^2 / \lambda_k \qquad (12)$$

since, in general, $F_{ij}L_{ij}L_{jk}$ is large only when $i = j$ (however, see footnote 10c). These diagonal terms, collectively referred to as the potential energy distribution (PED), provide a measure of each internal coordinate's contribution to the normal coordinate k and are available in the output of standard programs. Thus, the elements of the PED can be used to extract the vibrational energy associated with a given internal coordinate from the set of observed frequencies. In this way, it is possible to estimate the "pseudodiatomic" stretching frequency of a given bond in a polyatomic system.

$$E_j = \sum_{k=1}^{N} \mathrm{PED}_j^k \nu_k \qquad (13)$$

Equation 5 is then written as

$$\Delta r = (r_2 - r_1) = 0.408 \ln (E_{j1}/E_{j2}) = 0.408 \ln (\nu_{j1}/\nu_{j2}) \qquad (14)$$

i.e., the change in bond length is proportional to the natural logarithm of the ratio of the total vibrational energy of the jth coordinate in system 1 (ν_{j1}) to that in system 2 (ν_{j2}). We note that Boatz and Gordon[10a] and others[10b] have developed equations similar to eq 13 for the decomposition of normal coordinates.

For many types of transformations (e.g., comparing ground and excited states, anion radicals with the neutral parent, etc.), it is reasonable to consider contributions from only the bond-stretching coordinates. This approximation is justified on the basis of the results from several studies.[9] Thus, in those cases where a particular mode is known to be almost purely bending in character, only slight shifts are observed upon anion radical formation. In any case, the method described here is designed to extract the total energy of a given bond-stretching coordinate and does not require determination of the energy contributed by bending coordinates to arrive at a pseudodiatomic stretching frequency.

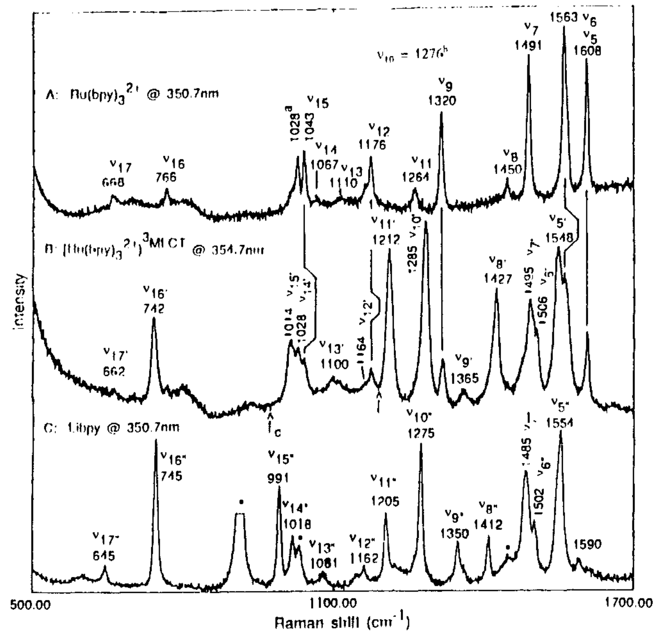

Figure 1. Resonance Raman and time-resolved Raman spectra: (A) 1028 cm^{-1} is depolarized; (B) ν_{10} = 1276 cm^{-1} is observed as a band with moderate intensity when ^{1}MLCT excitation is used (e.g., 457.9 nm); (C) region between arrows was obtained with use of higher resolution conditions. Bands belonging to the THF solvent are denoted by an asterisk.

Results and Discussion

Resonance Raman Spectra of Ru(bpy)$_3^{2+}$ and Its ^{3}MLCT Excited State. Resonance Raman and TR^3 spectra of Ru(bpy)$_3$ and its ^{3}MLCT state are especially useful for revealing the nature of the excited state.[5,7] For convenience, we have reproduced the RR spectra of the ground and ^{3}MLCT states in Figure 1. The essential features are as follows.

There is no vibrational interaction between the bipyridine ligands of the tris complex so that the system can be treated as a single coordinated-bipyridine fragment. This (C_{2v}) 21-atom unit gives rise to 20 in-plane, A$_1$ modes. Four of these are CH-stretching vibrations that are not resonance enhanced and are not of primary interest in deducing ^{3}MLCT-state structure. There are seven ring-stretching coordinates and four in-plane hydrogen-wagging coordinates that may couple to give rise to eleven modes between 1650 and 1000 cm^{-1}. These are labeled ν_5–ν_{15} in Figure 1 (trace A). Deuterium substitution at various positions will lower the number of modes occurring in the 1650–1000-cm^{-1} ring accordingly and also alter the mode compositions (e.g., the dideuteriated analogues will possess ten modes between 1650 and 1000 cm^{-1} and one CC^{2}H wag between 800 and 900 cm^{-1}). In conducting the NCA of the ground-state species, we employed eleven isotopically substituted analogues including the ^{15}N-labeled species as well as the doubly labeled [^{15}N$_2$]-3,3′-dideuterio-2,2′-bipyridine complex.[7]

As was first shown by Dallinger, Woodruff, and co-workers,[5] the TR^3 spectrum of Ru(bpy)$_3^{2+}$ is entirely consistent with a localized ^{3}MLCT state inasmuch as the spectrum is comprised of two sets of bands: one corresponding to the vibrations of a bipyridine anion radical and one being essentially identical with the ground-state bands. These latter bands are associated with the two remaining coordinated "neutral ligand" fragments. Thus, the ^{3}MLCT state is most properly formulated as [Ru^{3+}(bpy)$_2$(bpy$^-$)$^{2+}$. Such arguments are clearly supported by the spectra shown in Figure 1. The TR^3 spectrum (trace B) contains features (labeled ν_i') whose positions and relative intensities are closely matched with bands observed for the lithium bipyridine anion radical, Li(bpy) (trace C).[5,7,12] The similarity of the ν_i' features

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with the bands in trace C and the lack of perturbation of the neutral ligand modes in trace B (compared to those in trace A) argues strongly that the anion radical fragment Ru(bpy$^{\bullet-}$) can also be treated as an isolated vibrational unit. As in the case of the ground-state calculation, in conducting the NCA on the anion radical fragment of the ^{3}MLCT state, we employed data for eleven isotopically labeled analogues in addition to the (natural-abundance) parent complex.[7]

Normal-Coordinate Calculations for the Ground and ^{3}MLCT States. The details of our recently completed normal-coordinate calculations are reported elsewhere.[6,7] However, with respect to the goals of the present work, it is important to note several points regarding those calculations.

In deriving the force fields, an effort was made to limit the number of independent force constants. This was accomplished by expressing certain off-diagonal elements in terms of other off-diagonal elements rather than including them as independent force constants. This strategy accomplishes two important goals. First, it helps to prevent the evolution of physically unrealistic values for force constants during the mathematical adjustment procedure wherein calculated frequencies are fit to the observed. Second, such force fields, wherein off-diagonal elements are realistically interrelated (based on well-defined fields for simple molecules), are much more likely to be transferable to complexes of substituted bipyridines and related ligands: an important goal for extension to other systems.

While these important objectives are accomplished with such force fields, it is also true that some flexibility is lost that prevents highly precise reproduction of the observed frequencies. Nevertheless, this was not judged to be a severe restriction in that the observed frequencies of twelve isotopomers were reproduced with average errors of ~1% for both electronic states. Also, it is especially satisfying that the observed ^{15}N shifts for both states were well-reproduced for both cases studied; i.e., comparing shifts for $Ru(bpy)_3{}^{2+}$ vs $Ru([^{15}N_2]bpy)_3{}^{2+}$ as well as for $Ru([3,3'\text{-}{}^2H_2]bpy)^{2+}$ vs $Ru([3,3'\text{-}{}^2H_2,{}^{15}N_2]bpy_3{}^{2+})$.[7]

Finally, we emphasize that, when the ^{3}MLCT-state force field is derived, no assumptions were made regarding ^{3}MLCT-state structure. As is discussed in detail elsewhere,[7] the ^{3}MLCT-state stretching force constants were assigned initial values of 5.8 and 5.4 mdyn/Å for the C–C and C–N bonds, respectively (i.e., all C–C bonds were considered to be equivalent). The angle-bending force constants and the stretch–bend interaction constants were fixed at the values derived for the ground-state calculation, as these are not expected to change substantially upon ^{3}MLCT-state formation.[9] With this set of initial (unbiased) stretching force constants, the fitting to the observed frequencies was accomplished with only an iterative calculational procedure, with no manual adjustments being made.

Inasmuch as our primary objective is to utilize ground and ^{3}MLCT force fields to relate vibrational frequency data to ^{3}MLCT-state structural changes, it is important that the derived force fields correctly reproduce the observed vibrational frequency shifts upon ^{3}MLCT-state formation. As is shown in detail elsewhere,[7] these shifts were well-reproduced for all of the isotopomers studied.

In summary, the observed isotopic shifts and the observed $\Delta\nu$ values (ground- to ^{3}MLCT-state frequency shifts) were well-reproduced by the derived force fields. These features instill confidence in the general validity of the derived fields and provide encouraging evidence that they may be successfully applied to problems concerning structure and dynamics. While the inclusion of additional force constants and removal of the minor restrictions (i.e., disconnecting off-diagonals) may provide a slightly better fit to the observed frequencies, it is not likely that the essential composition of the modes (i.e., the PED's) would change significantly.

The full PED's for the ground and ^{3}MLCT states of $Ru(bpy)_3{}^{2+}$ have been previously reported.[7] Those for isotopically labeled analogues are available from us upon request. For the present purpose it is only necessary to consider the contributions of the seven bond-stretching coordinates. These are summarized in Table I along with the observed frequencies, for both the ground and ^{3}MLCT states, for the (natural-abundance) parent complex.

Estimated ^{3}MLCT-State Structural Changes. The data given in Table I can be used, along with the known structure of the ground state,[13a] to calculate (via eq 14) the bond length changes associated with ^{3}MLCT-state formation (i.e., the bond length changes in the ^{3}MLCT-state anion radical fragment relative to the bond lengths of a neutral coordinated bipyridine). Thus, in Table I we have also listed the pseudodiatomic stretching frequencies for a given bond-stretching coordinate for both the ground (ν_{PD}) and ^{3}MLCT states (ν_{PD}'). For example, the value of 1135 cm^{-1} given for $\nu_{PD}(C_2\text{–}C_{2'})$ was obtained from the sum of $\nu_i \times PED_i$ for mode numbers 5–20, i.e., (1608 cm^{-1} × 0.034) + (1556 cm^{-1} × 0.009) + (1491 cm^{-1} × 0.259), etc. Similarly, a value of $\nu_{PD}'(C_2\text{–}C_{2'}) = 1275$ cm^{-1} was obtained by applying this procedure to the PED's given for the ^{3}MLCT-state anion radical fragment. These two pseudodiatomic stretching frequencies are then used in eq 14 to yield a calculated $\Delta r(r_{^3MLCT} - r_{GS}) = -0.048$ Å. The calculated Δr values, obtained via eq 14 for each of the seven bonds, are given in Table II and are labeled as Δr_{HL} (to indicate that the value is derived with Herschbach and Laurie's[2] empirical constant, $b_{ij} = 0.47$). We have also calculated the bond length changes (labeled Δr_J) using the empirical constant given by Johnston,[8] $b_{ij} = 0.55$.

In addition, we have calculated Δr values for five specifically deuteriated analogues (Table III). The excellent agreement of the calculated Δr values among the isotopcially substituted analogues instills some confidence in the procedure in the following sense. Selective deuteration causes substantial changes in the compositions of the vibrational modes. Thus, a particular mode may exhibit a shift to higher frequency upon ^{3}MLCT-state formation for one isotopomer while exhibiting a shift to lower frequency for a different isotopomer. The fact that the derived PED's for the various isotopomers can be used in combination with the corresponding ground- and ^{3}MLCT-state frequencies to yield consistent values for Δr lends confidence not only to the reliability of the normal-mode formulations but also to the validity of the procedure that generates pseudodiatomic stretching frequencies.

Obviously, it is possible to use the values of the ground- and ^{3}MLCT-state force constants to calculate Δr values via eq 3. However, certain advantages attend employment of the PED's and experimental frequencies. First, the derived force constants contain some degree of uncertainty. Direct utilization of these will produce a porportionally large error in the calculated Δr. However, small variations in diagonal force constant values are not likely to produce substantial errors in the PED components. The utilization of these components with the actual experimental frequencies will generally lead to lower errors in the calculated Δr values. For the purpose of illustration, Δr values calculated from the previously reported force constants[7] are listed in Table II (labeled Δr_F). As will be discussed later, the Δr_F values are less satisfactory than those calculated with eq 14. Finally, provided the PED's do not change significantly (vide infra), the data in Table I can be employed directly to extract structural differences in situations where the system is only slightly perturbed. For example, relatively small frequency shifts induced by environmental effects could be directly converted to estimated bond length changes.

Normal-Mode Formulations and the Effect of Missing Frequencies. Clearly, in order to utilize the procedure described here, an extensive body of vibrational data must be acquired. The principal requirement is that reliable estimates of the normal modes are obtained for both of the species being compared. In the present case, inspection of Table I reveals substantial differences in the ground- and ^{3}MLCT-state normal-mode compositions. In fact, it is instructive to compare the Δr values calculated with only the *ground-state* PED components for both states. The resulting Δr values (labeled Δr_{gsgs} in Table II) are considerably

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Table I. Ground- and ^{3}MLCT-State Frequencies and Potential Energy Distributions[a]

	obs[b]	$\nu(C_2–C_{2'})$	$\nu(C_2–N)$	$\nu(C_2–C_3)$	$\nu(C_3–C_4)$	$\nu(C_4C_5)$	$\nu(C_5–C_6)$	$\nu(C_6–N)$
ν_5	1608	0.034	0.016	0.104	0.078	0.490	0.020	0.023
$\nu_{5'}$	1548	0.015	0	0.058	0.334	0.013	0.221	0.098
ν_6	1563	0.009	0.005	0.149	0.251	0	0.300	0.100
$\nu_{6'}$	1506	0.394	0.017	0.156	0	0.122	0.002	0.016
ν_7	1491	0.259	0.084	0.172	0.060	0.059	0.184	0.003
$\nu_{7'}$	1495	0.131	0.180	0.005	0.024	0.255	0.173	0.041
ν_8	1450	0.001	0.059	0.042	0.118	0.007	0.006	0.105
$\nu_{8'}$	1427	0.052	0.008	0.011	0.224	0.018	0.054	0.104
ν_9	1320	0.316	0.005	0.016	0.028	0.004	0.013	0.001
$\nu_{9'}$	1365	0.138	0.030	0.035	0.054	0.005	0.085	0
ν_{10}[c]	1276	0.016	0.380	0.364	0.109	0.121	0.133	0.203
$\nu_{10'}$	1285	0.034	0.332	0.232	0.080	0.139	0.129	0.171
ν_{11}	1264	0.023	0.006	0.009	0	0.006	0.014	0.237
$\nu_{11'}$	1212	0.002	0.006	0.001	0.009	0.002	0.023	0.203
ν_{12}	1176	0	0.036	0.004	0.014	0.007	0.004	0.019
$\nu_{12'}$	1164	0	0.022	0.001	0.020	0.008	0.015	0.006
ν_{13}	1110	0.012	0	0.019	0.137	0.003	0.u04	0.111
$\nu_{13'}$	1100	0.004	0.031	0.069	0.090	0.003	0.129	0.132
ν_{14}	1067	0	0.127	0.013	0.048	0.177	0.033	0.001
$\nu_{14'}$	1028	0.022	0.122	0.057	0.009	0.107	0.015	0.018
ν_{15}	1043	0.052	0.092	0.029	0.105	0.110	0.175	0.061
$\nu_{15'}$	1014	0.050	0.003	0.036	0.094	0.283	0.125	0.044
ν_{16}	776	0.062	0.134	0.121	0	0.004	0.018	0.006
$\nu_{16'}$	742	0.017	0.135	0.255	0	0.015	0.021	0.004
ν_{17}	668	0	0.112	0.006	0	0.034	0.013	0.013
$\nu_{17'}$	[664]	0	0.118	0.002	0	0.055	0.016	0.024
ν_{18}	370	0.200	0.017	0.037	0.048	0.003	0.002	0.123
$\nu_{18'}$	[355]	0.144	0.029	0.066	0.045	0.002	0.002	0.127
ν_{19}	283	0.020	0.050	0.007	0	0	0	0.025
$\nu_{19'}$	[269]	0.015	0.048	0.019	0	0	0	0.016
ν_{20}	[188]	0.066	0	0	0.037	0	0.020	0.006
$\nu_{20'}$	[189]	0.048	0	0	0.032	0	0.019	0.008
ν_{PD}		1135	1217	1397	1310	1394	1352	1187
$\nu_{PD'}$		1275	1171	1178	1308	1256	1324	1136

[a] Values given are the fractional PED's (e.g., the contribution of $\nu(C_2–C_{2'})$ to ν_5 is 3.4%). [b] Observed frequencies. [c] This mode contains an unexpectedly large contribution from off-diagonal elements (see ref 7 for a discussion).

Table II. Bond Lengths and Bond Length Changes

symbol	$C_2–C_{2'}$	$C_2–N$	$C_2–C_3$	$C_3–C_4$	$C_4–C_5$	$C_5–C_6$	$C_6–N$	remarks
				Vibrational Frequency Determination				
Δr_{HL}	−0.048	0.016	0.070	0	0.043	0.009	0.018	calcd with $b_{ij} = 0.47$
Δr_J	−0.056	0.018	0.082	0.001	0.050	0.010	0.021	calcd with $b_{ij} = 0.55$
Δr_F	−0.040	0.004	0.059	−0.003	0.045	0.008	0.010	calcd with force constants and eq 3: $b_{ij} = 0.47$
$\Delta r_{gs,gs}$	−0.002	0.004	0.005	0.008	0.012	0.008	0.009	calcd with ground-state PED for ^{3}MLCT state; $b_{ij} = 0.47$
$\Delta r(\nu_8,\nu_8')$	−0.048	0.015	0.069	0	0.042	0.008	0.17	calcd with calcd ν_8 and ν_8'; $b_{ij} = 0.47$
Δr_{12}	−0.062	0.019	0.074	0	0.048	0.009	0.021	calcd with only ν_5–ν_{16}; $b_{ij} = 0.47$
				X-ray Crystal Structure Determination				
r_{Ru}	1.476	1.355	1.363	1.376	1.347	1.365	1.351	ref 13a
r_{bpy}	1.4767	1.353	1.394	1.384	1.380	1.390	1.348	ref 13b
r_{Mo}	1.417	1.380	1.409	1.370	1.406	1.368	1.371	ref 14a
r_{Fe}	1.424	1.383	1.412	1.365	1.415	1.358	1.376	ref 14b
Δr(Mo–Ru)	−0.059	0.025	0.046	−0.006	0.059	0.003	0.020	
Δr(Mo–bpy)	−0.050	0.027	0.015	−0.014	0.026	−0.022	0.023	
Δr(Fe–Ru)	−0.052	0.028	0.049	−0.011	0.068	−0.007	0.025	

Table III. Calculated Bond Length Changes (Å) for Isotopically Labeled Complexes

isotopomer	$C_2–C_{2'}$	$C_2–N$	$C_2–C_3$	$C_3–C_4$	$C_4–C_5$	$C_5–C_6$	$C_6–N$
$^1H_8$	−0.048	0.016	0.070	0	0.043	0.009	0.018
3,3'-$^2H_2$	−0.046	0.016	0.066	0	0.042	0.008	0.016
4,4'-$^2H_2$	−0.048	0.015	0.069	0.001	0.042	0.008	0.016
5,5'-$^2H_2$	−0.048	0.015	0.069	0	0.040	0.010	0.017
6,6'-$^2H_2$	−0.048	0.015	0.069	0	0.042	0.008	0.016
$^2H_8$	−0.048	0.016	0.068	0.003	0.042	0.009	0.016

different from the Δr_{HL} values. This disparity emphasizes the need to obtain reasonably reliable estimates of normal-mode compositions for both "molecules" of interest (i.e., both electronic states or redox partners).

Even in the situation where the sets of vibrational data are sufficient to obtain reliable PED's, minor complications can be encountered. Thus, in the present case, many of the low-frequency modes of the ^{3}MLCT state are not observed. One solution is to employ calculated frequencies for one or two nonobserved modes. As long as the PED's are reasonably accurate, this should not introduce significant error. For example, if the calculated frequencies for ν_8 and $\nu_{8'}$ are used in the present case, the Δr values, labeled $\Delta r(\nu_8,\nu_{8'})$ in Table II, are not significantly different from those obtained with use of the observed frequencies.

The absence of observed frequencies in the low-frequency region is not expected to introduce severe complications inasmuch as stretching coordinates, in general, do not make substantial contributions to these modes. In fact, the bond length changes (labeled Δr_{12} in Table II) obtained when these modes are omitted entirely (i.e., only twelve frequencies are used) are only slightly different from the Δr_{HL} values, the largest error occurring for the C_2–$C_{2'}$ bond that does make moderate contributions to $\nu_{18}/\nu_{18'}$ and $\nu_{19}/\nu_{19'}$.

Comparison of Calculated Structure with Expectation. Experimental[14] and theoretical[15] studies have been reported that serve to qualitatively describe the bond length changes that are expected to accompany ^{3}MLCT-state formation. Briefly, the results of molecular orbital calculations conducted by Kober and Meyer[15] predict a large decrease for the C_2–$C_{2'}$ bond length and smaller decreases for the C_3–C_4 and C_5–C_6 bonds. All other bonds are predicted to lengthen, especially the C_2–C_3 and C_4–C_5 bonds.

The experimental data that are most relevant to this issue are the crystal structure determinations of the "^{3}MLCT-state models", $Mo(bpy)_2(i\text{-}PrO)_2$[14a] and $Fe(\eta^6\text{-}C_7H_8)(bpy)$.[14b] These are low oxidation state complexes in which extensive d π–bpy π^* back-bonding places substantial electron density in the lowest bpy π^* orbital. The measured bond lengths for these two complexes are given in Table II (labeled as r_{Mo} and r_{Fe}, respectively). The measured bond lengths for $Ru(bpy)_3^{2+}$[13a] are also given in Table II (labeled r_{Ru}). For the sake of completeness, we have also included the average bond lengths for a typical coordinated bipyridine that were derived[13b] from a compilation of X-ray structure data for 128 "normal" bipyridine complexes (labeled r_{bpy} in Table II).

With the various crystal structure determinations, a number of sets of "experimental" Δr values are derived (labeled Δr(Mo–Ru), Δr(Fe–Ru), Δr(Mo–bpy), etc., in Table II). It is probably most appropriate to compare Δr_{HL} and Δr_J with Δr(Mo–Ru) values (i.e., those derived with the crystal structure determination for $Ru(bpy)_3^{2+}$). As can be seen by inspection of these rows in Table II, quite satisfactory agreement is obtained. Thus, the vibrational frequency determinations and the crystal structure determinations indicate a *decrease* for the C_2–$C_{2'}$ bond length of ~0.05–0.06 Å. The small decrease for the C_3–C_4 bond length obtained from the structure determination is given as a very small *increase* by the vibrational frequency data (i.e., both types of determination indicate an insignificant change). Both methods indicate a very slight increase in the C_5–C_6 bond length. While both determinations indicate large increases for the C_2–C_3 and C_4–C_5 bond lengths, the relative order is reversed; i.e., the determination from vibrational frequency data indicates a larger increase for the C_2–C_3 bond. Finally, both sets show increases for the C–N bonds of ~0.02 Å.

Perhaps the most important difference between the Δr_{HL} (or Δr_J) values and the Δr(Mo–Ru) values is the reversal involving $\Delta r(C_2\text{–}C_3)$ and $\Delta r(C_5\text{–}C_6)$, the vibrational frequency determination, indicating a larger increase for the C_2–C_3 bond. While it is true that slight errors[16] in the derived PED's may lead to such structural "errors", it is obviously possible that real differences exist between the true ^{3}MLCT-state structure and the model compounds. While further definition of Δr values from vibrational frequency data would be aided by acquisition of the RR spectra of heavy-atom isotopically labeled complexes (e.g., $[4,4'\text{-}^{13}C_2]$-2,2'-bipyridine), such species are not currently available.

Conclusion

The present work demonstrates the utility of extensive vibrational frequency data for the quantitative determination of structural parameters of transient species. For the example discussed here, the resulting Δr values are shown to be entirely consistent with predictions based on both theoretical and model compound studies. The relatively minor differences between the calculated Δr values and those derived from the model compound data are not necessarily ascribable to errors in the method but may simply be the consequence of actual differences in the ^{3}MLCT-state structure of $Ru(bpy)_3^{2+}$ from those of the molybdenum and iron model compounds.

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(16) As is discussed in detail in ref 7, the PED values for certain modes (especially ν_{10}) contain slightly larger contributions from off-diagonal elements than is expected.