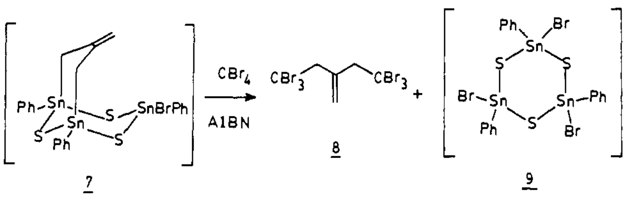
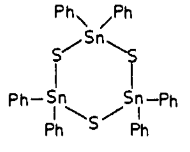
chlorides.[13] Trimethyltin chloride was not reduced, suggesting that the central carbon–hydrogen bond of stannaadamantane **4** is stronger than a representative tin–hydrogen bond.

Since these reductions are accelerated by AIBN, we believe that the central carbon–hydrogen bond of compound **4** is cleaved homolytically, producing radicals **5** or **6** (Scheme I). Allylstannanes **7** are then formed by abstraction of halogen.[14] These reactive compounds could not be isolated, but evidence for their formation comes from the following experiment. When allylstannane **7** (X = Br) was warmed with excess carbon tetrabromide (benzene, AIBN, 95 °C), 1,1,1,5,5,5-hexabromo-3-methylenepentane (**8**)[8,15] was formed in 60% overall yield by a reaction characteristic of allylstannanes.



The reductions of alkyl halides by stannaadamantane **4** are similar to dehalogenations effected by tin hydrides.[16] However, we doubt that compound **4** is actually converted into a tin hydride, since it is stable in the absence of reducible substrates, and no additions to carbon–carbon or carbon–oxygen double bonds have been observed. We therefore attribute the reactivity of stannaadamantane **4** to its unusual central carbon–hydrogen bond. Related compounds that lack this feature are in fact inert.[17] For example, trithiatristannacyclohexane **10** did not reduce 1,2-dibromoethane, nor did bis[(triphenylstannyl)methyl]methane (**11**)[3b] reduce α-bromoacetophenones in the presence of AIBN.



10

$Ph_3SnCH_2CH_2CH_2SnPh_3$

11

The central carbon–hydrogen bond in stannaadamantane **4** is an unusually reactive source of hydrogen, comparable in some respects to a tin–hydrogen bond. The efficient and selective reductions of alkyl halides by stannaadamantane **4** suggest that related, more accessible compounds may prove to be synthetically useful.

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Registry No. 2, 87549-81-3; **3**, 88563-24-0; **4**, 87922-35-8; **7**, 88563-23-9; **8**, 88563-25-1; α-bromo-*p*-phenylacetophenone, 135-73-9; triphenylmethane, 519-73-3; *p*-phenylacetophenone, 92-91-1; triphenylcarbenium hexafluorophosphate, 437-17-2.

Supplementary Material Available: Spectroscopic and analytical data for all new compounds (1 page). Ordering information is given on any current masthead page.

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Excited-State Distortions from Resonance Raman Overtone Intensities in $K_3[Cr(CN)_5NO]$

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Displacements of potential surfaces of excited electronic states relative to the ground-state surface are of fundamental importance in spectroscopy, photophysics, and photochemistry. The magnitudes of such displacements along specific normal modes are usually calculated from Franck–Condon factors.[1] Recently the multimode displacements in transition-metal complexes were calculated using the intensities of fundamentals in Raman spectra.[2-6] In principle, resonance Raman *overtone* intensities can provide complementary information, but in practice they rarely exhibit significant intensity in polyatomic molecules with many displaced normal modes.[3]

During the course of our studies of the excited-state properties of metal nitrosyl compounds, we discovered that the $Cr(CN)_5NO^{3-}$ ion possesses almost ideal spectroscopic characteristics for determining excited-state distortions from Raman overtone intensities. There are a relatively small number of significantly displaced normal modes, thus giving both a relative large overtone intensity (18% of that of the fundamental) and concomitantly enough fundamentals to provide a cross-check of the calculation. In addition, the electronic absorption spectrum exhibits enough vibronic structure at low temperature[7] to enable the E_{00} band to be observed and thus allow accurate tuning of the laser to exact resonance with the electronic origin. The successful calculation of the absorption spectrum from the Raman-determined displacements provides a second cross-check. We report here the first calculation of the displacement of a potential surface along a given normal mode in a multimode, polyatomic transition-metal complex from the intensity of its overtone.

The displacement of Δ_k of the excited-state potential surface along the kth normal model of frequency ω_k is given by[3]

$$\Delta_k^2 = \frac{I_{20}^k}{I_{10}^k}\frac{4\sigma^2}{\omega_k^2}\frac{\epsilon_1((W_I - E)/\sigma)}{\epsilon_2((W_I - E)/\sigma)} \qquad (1)$$

I_{20}^k/I_{10}^k is the intensity ratio of the overtone to the fundamental, σ^2 is related to the absorption bandwidth, and ϵ_n is a function based on the energy difference between the absorption band maximum and the laser Raman excitation.[3]

The resonance Raman and electronic absorption spectra are shown in Figure 1. By use of the first overtone intensity (Table I), the absorption spectral line width, and an ϵ_1/ϵ_2 ratio of 0.752, the displacement along the Cr–N stretching normal mode calculated by eq 1 is 2.20. (On the assumption that this coordinate is puely the uncoupled M–N stretch, this displacement is 0.09 Å.) As a check, the displacement along this normal coordinate is calculated from the intensities of the fundamentals by using methods previously described.[2-6] The displacement calculated by these complementary methods is 2.60 (~0.10 Å). The two calculated displacements agree within experimental error.

The value of the Raman methods for determining the displacement is especially apparent because the usual Franck–Condon calculation is not feasible. The electronic absorption band (as-

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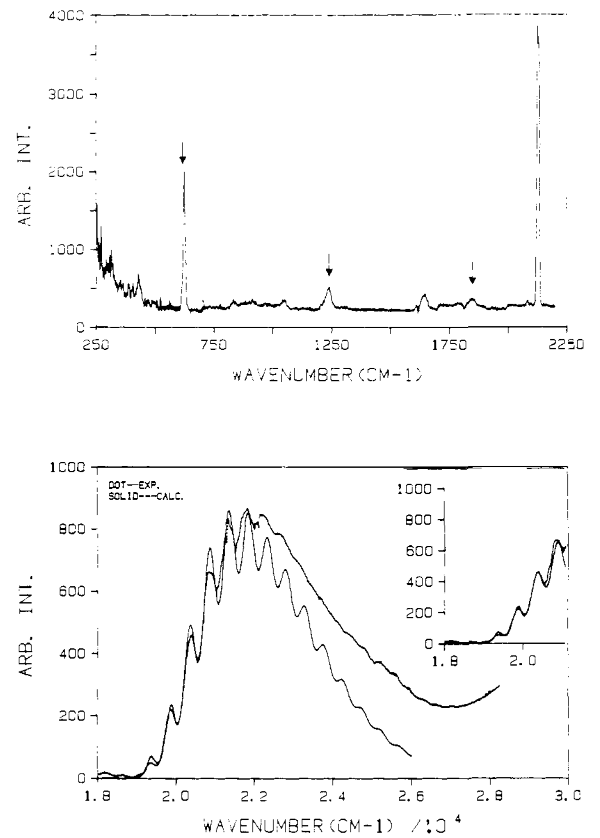

Figure 1. (Top) Raman spectrum of K_3 $Cr(CN)_5NO$ excited at 514.5 nm. The arrows indicate the fundamental and first and second overtones of the Cr–N stretching mode. (Bottom) Experimental (dots) and calculated (solid) electronic absorption spectra. Note the presence of a shoulder at 25 000 cm^{-1} and the tail of the next peak at 28 000 cm^{-1}. The spectrum was calculated using $\Gamma = 93$ and the following frequencies and displacements: 400, 1.60; 530, 2.60; 1500, 0.26; 1900 cm^{-1}, 0.80. The insert shows the region near the origin and the spectrum calculated by using *exactly* the Raman-determined displacements, $\Gamma = 105$, and frequencies of 400, 530, 1645, and 2128 cm^{-1}.

Table I. Raman Intensities and Calculated Distortions

ω_k, cm^{-1}	assignment	I_k/I_{624} [b]	Δ_k [c]	Δ_k, [d] Å
428	ν_{CrC} [a]	0.13 ± 0.03	1.37 ± 0.30	0.07
624	ν_{CrN} [a]	1.00 ± 0.20	2.60 ± 0.50	0.10
1645	ν_{NO} [a]	0.07 ± 0.01	0.26 ± 0.05	0.01
2128	ν_{CN} [a]	1.42 ± 0.28	0.90 ± 0.20	0.03
1237	1st overtone	0.18 ± 0.04	2.20 ± 0.40	0.09
1848	2nd overtone	0.09 ± 0.02	N/A	N/A

[a] Assignment from ref 7. [b] Integrated intensity ratios from 514.5-nm excitation. The intensity ratio of the overtone to fundamental is 0.30 when excited at 488 nm. The calculated displacement is 2.0 ± 0.4. The overtone was too weak to be observed under 632.8- and 647.1-nm excitation. [c] Dimensionless normal coordinates. [d] Displacements in Å assuming uncoupled normal modes. More accurate values require a normal coordinate analysis.

signed by Gray et al. to the $^2B_2 \rightarrow {}^2B_2$, metal to NO charge transfer)[7] exhibits resolved vibronic structure. However, the spacing between the vibronic features is not regular. Furthermore, the band is overlapped by additional bands on its high-energy side, which are revealed by polarization studies. The low-energy features of the electronic spectrum, which are unemcumbered by the overlapping bands, can be calculated from the Raman-determined displacements.[4-6] The calculation uses time-dependent theory and the multidimensional excited-state surface obtained from the Raman-determined displacements. An excellent fit to the low-energy features was achieved by using *exactly* the displacements determined from the Raman intensities for the four normal modes. The vibronic features are thus a result of all of the displaced normal modes (i.e., a type of MIME[6,8]) and not the result of a single mode. The calculated electronic spectra provide a further check and verify the accuracy of the Raman-determined displacements.

These results show that overtone intensities can be reliably used to calculate excited-state displacements. These data also shed light on the underlying mechanism giving rise to the overtone intensity. Of the two possible limiting mechanisms derived from time-dependent theory, displaced excited states or vibrational frequency changes in excited states,[3] the former is over 2 orders of magnitude more important than the latter for $Cr(CN)_5NO^{3-}$. Ziegler and Albrecht have discussed seven origins of overtone intensity and have shown that the displaced excited-state mechanism is expected to become important as resonance is approached.[9] The calculation of excited-state displacements from overtone intensities is a new tool in the study of the electronic structure of metal complexes.

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Registry No. $K_3Cr(CN)_5NO$, 14100-08-4.

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Mechanism of the Irreversible Deactivation of Arachidonate 5-Lipoxygenase by 5,6-Dehydroarachidonate

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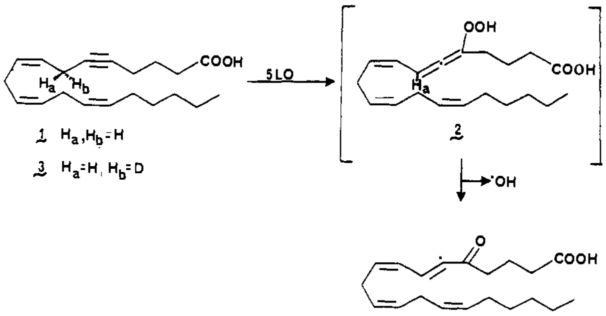
The initial step in leukotriene biosynthesis, conversion of arachidonate to a 5-hydroperoxytetraenoic acid by a 5-lipoxygenation (5-LO) reaction can be inhibited irreversibily in vitro and in whole cells by micromolar concentrations of 5,6-dehydroarachidonate (**1**).[1-5] The time dependence of the degree of inhibition and the requirement of both Ca^{2+} and O_2, each of which is needed for the 5-LO reaction of arachidonate, support the hypothesis that 5-LO inactivation is due to oxidation of **1** to a vinylic hydroperoxide **2** which rapidly decomposes to radicals capable of lethal damage to the catalytic site. The argument is further strengthened by the finding that 4,5-dehydroarachidonate, an allenic isomer of **1**, causes inactivation of the 5-LO enzyme in the same manner as does **1**.[6] In this communication we show that the rate of 5-LO



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