

We are now in position to estimate the ground-state Rh-Rh bond energy in $\text{Rh}_2\text{b}_4^{2+}$ from the following relationship: $D_e(^1A_{1g}) = E_t^d(^3A_{2u} \leftarrow ^1A_{1g}, \text{Rh}_2^{2+}) - E_t^m(^3A_{2u} \leftarrow ^1A_{1g}, \text{Rh}^+) + D_e(^3A_{2u})$. From the spectrum of $\text{Rh}(\text{CNR})_4^+$ we take $E_t^m = 62$ kcal/mol⁸ and E_t^d for $\text{Rh}_2\text{b}_4^{2+} = 38$ kcal/mol. Thus for $D_e(^3A_{2u}) = 42$ kcal/mol, the ground-state Rh-Rh bond energy is about 18 kcal/mol. Because the 0-0 energies of the triplet \leftarrow singlet transitions are known quite accurately, any error in $D_e(^1A_{1g})$ must come from the Birge-Sponer value for $D_e(^3A_{2u})$. Accordingly, we consider 18 kcal/mol as an upper limit for the ground-state Rh-Rh bond energy, as it is likely that the Birge-Sponer extrapolation overestimates¹⁴ $D_e(^3A_{2u})$ for $\text{Rh}_2\text{b}_4^{2+}$. We intend to study the temperature dependence of the dissociation of $\text{Rh}_2(\text{CNR})_8^{2+}$ complexes in various solvents, which should provide additional information on this point.

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(15) Because the bridging ligands will prevent Rh-Rh dissociation, the estimated D_e is for the $^3A_{2u}$ state of a strictly analogous unbridged complex, $\text{Rh}_2(\text{CNR})_8^{2+}$. Interestingly, the Birge-Sponer plot [E_v/v vs. v (Clark, R. J.; Franks, M. L. *J. Am. Chem. Soc.* 1976, 98, 2763)] exhibits a significant curvature, suggesting that the decrease in vibrational frequency per vibrational quantum begins to level off. It is our opinion that this curvature represents mixing of ligand bending character into the Rh-Rh stretching wave function for high a_{1g} vibrational quanta. The value of χ_e was obtained from fitting only the first 10 vibrational quanta to a straight line, thereby approximating an unbridged Rh-Rh bond.

Metal-Metal Interactions in Binuclear Rhodium Isocyanide Complexes. Resonance Raman Spectra of the $^1A_{1g}$ and $E_u(^3A_{2u})$ Electronic States of Tetrakis(1,3-diisocyanopropane)dirhodium(I)

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The unique photophysical and photochemical properties of binuclear rhodium(I) isocyanide complexes have received much recent attention.²⁻⁹ There is some Rh-Rh bonding interaction in the ground state ($^1A_{1g}$) of the prototypal complex, $\text{Rh}_2\text{b}_4^{2+}$ ($\text{b} = 1,3$ -diisocyanopropane), in spite of the fact that simple theory suggests that the Rh-Rh bond order is zero (filled $4d_{z^2}\sigma$ and $4d_{z^2}\sigma^*$ orbitals).⁹ Greatly enhanced Rh-Rh bonding is predicted for the lowest triplet and singlet excited states, owing to the promotion

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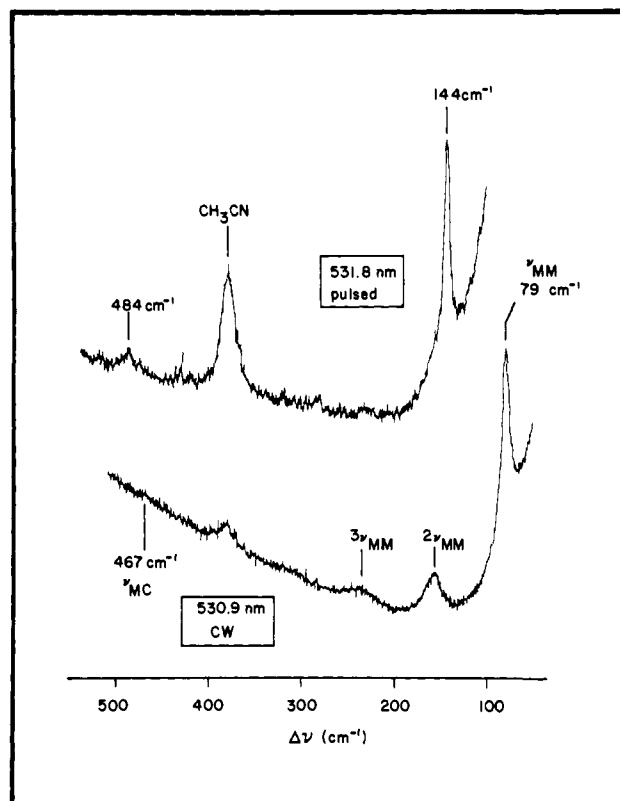


Figure 1. Lower trace: ground-state resonance Raman spectrum of $\text{Rh}_2\text{b}_4^{2+}$ obtained by continuous-wave excitation at 530.9 nm (Kr laser). Conditions: laser power, 75 mW at the sample; $[\text{Rh}_2\text{b}_4^{2+}] = 5 \times 10^{-4}$ M in CH_3CN solvent. The acetonitrile was filtered through activated charcoal, then deaerated by bubbling nitrogen followed by three cycles of freeze-pump-thaw. Upper trace: excited-state resonance Raman spectrum of $\text{Rh}_2\text{b}_4^{2+}$ obtained by pulsed excitation with the second harmonic of the Q-switched Nd:YAG laser, 531.8 nm. The solution sample was the same as used for the ground-state spectrum. Excitation conditions: pulsed excitation at 531.8 nm, pulse duration 7 ns, per pulse energy 5 mJ, pulse repetition frequency 10 Hz, average (C.W. equivalent) power 50 mW.

of a $4d_{z^2}\sigma^*$ electron to a $5p_z\sigma$ orbital.² Measurement of the Rh-Rh vibrational frequencies in the ground and excited electronic states in question should reveal whether or not the Rh-Rh bonding is stronger in the latter. We report the results of such a study of the $^1A_{1g}$ and $E_u(^3A_{2u})$ states of $\text{Rh}_2\text{b}_4^{2+}$, using time-resolved resonance Raman (TR³) spectroscopy.

The TR³ technique¹⁰ has been successfully applied to several excited-state transients.¹¹⁻¹³ The experiment involves the creation of the desired excited state by optical or radiolytic excitation, with simultaneous or subsequent interrogation of the resonance Raman spectrum by using a pulsed laser. Acetonitrile solutions of $\text{Rh}_2\text{b}_4^{2+}$ (ca. 5×10^{-4} M) were deaerated with nitrogen prior to the pulsed Raman experiments. The laser excitation sources for the CW and pulsed resonance Raman experiments were the 530.9-nm line of a Spectra Physics 171 Kr⁺ laser and the 531.8-nm second harmonic of a Quanta-Ray DCR-1A Nd:YAG oscillator/amplifier, respectively. In both cases a spinning cell following the Shriver design was employed.¹⁴

The transient absorption difference spectrum of $\text{Rh}_2\text{b}_4^{2+}$ shows broad features [400-550-nm region, $\epsilon(\text{calcd}) \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$] to the blue of the ground-state absorption (553 nm) and prompt

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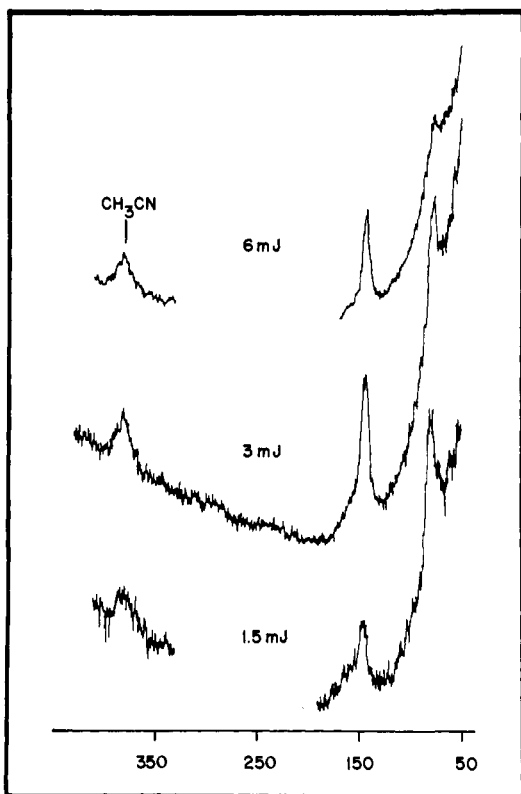


Figure 2. Dependence of the pulse-excited (531.8 nm, 7 ns pulses) spectrum of $\text{Rh}_2\text{b}_4^{2+}$ upon per pulse laser energy. Note that the intensity of the ground-state metal-metal stretching mode (79 cm^{-1}) diminishes relative to the excited-state metal-metal stretch (144 cm^{-1}) with increasing per pulse energy, therefore with increasing excited-state saturation. Pulse energy: lower trace, 1.5 mJ; middle trace, 3.0 mJ; upper trace, 6.0 mJ.

fluorescence (656 nm). These features have been assigned to allowed transitions of the $E_u(^3A_{2u})$ state ($\tau \sim 8.5\ \mu\text{s}$) involving distortion along the Rh-Rh coordinate. Excitation at 531.8 nm , where these transitions have considerable absorption intensity, is expected to result in large resonance Raman intensity enhancements of the Rh-Rh stretching vibration.

The singlet ($^1A_{2u}$) lifetime was determined to be less than $\sim 2\text{ ns}$, and the quantum yield for intersystem crossing was found to be large [$\Phi(\text{isc}) \sim 0.8$]. Thus, during our 7-ns Nd:YAG laser pulse, the major species present is the $E_u(^3A_{2u})$ state of $\text{Rh}_2\text{b}_4^{2+}$. Decay of this excited state to the ground state is complete in the 100 ms between laser pulses.

The $^1A_{1g}$ and $E_u(^3A_{2u})$ resonance Raman spectra of $\text{Rh}_2\text{b}_4^{2+}$ are shown in Figure 1. The ground-state spectrum (lower trace) shows an intense peak at 79 cm^{-1} with two overtones and a weak feature at 467 cm^{-1} . The 79-cm^{-1} band is clearly attributable to the Rh-Rh stretching motion, on the basis of its huge resonance enhancement [$\sim 10^5$ times (mol/mol) the acetonitrile intensity] and depolarization ratio of $\sim 1/3$. The 467-cm^{-1} band is assigned to the Rh-C stretch. It shows a smaller resonance enhancement, which is consistent with its assignment as a vibration orthogonal to the Rh-Rh axis.

The upper curve of Figure 1 shows the excited-state TR³ spectrum of the same solution of $\text{Rh}_2\text{b}_4^{2+}$. The principal feature of this spectrum is the intense band at 144 cm^{-1} , with an overtone at $\sim 284\text{ cm}^{-1}$ and a weaker peak at 484 cm^{-1} . The 144-cm^{-1} feature is attributable to the excited-state Rh-Rh stretch (vide infra), and the 484 cm^{-1} band is assigned as the excited-state Rh-C stretch. This TR³ spectrum is independent of the $\text{Rh}_2\text{b}_4^{2+}$ counterion (ClO_4^- , BPh_4^- , CF_3SO_3^-), and it is also independent of the solvent (CH_3CN , DMF).

The TR³ spectra of $\text{Rh}_2\text{b}_4^{2+}$ as a function of per pulse laser energy at 531.8 nm (Figure 2) confirm the assignment of the 144-cm^{-1} vibration as the excited-state Rh-Rh stretch. When the incident per pulse laser energy was varied from 1.5 to 6

mJ/pulse, the 144-cm^{-1} peak increased in intensity as the 79-cm^{-1} intensity decreased. This observation is independent of the order in which the spectra were taken and is entirely reversible, clearly correlating the $79\text{-} (^1A_{1g})$ and 144-cm^{-1} [$E_u(^3A_{2u})$] vibrational modes.

The observed increase in the Rh-Rh stretching frequency from $79\text{ } (^1A_{1g})$ to 144 cm^{-1} [$E_u(^3A_{2u})$] corresponds to *greater than a factor of 3* increase in the restoring force for this normal mode in the excited state. Owing to ligand contributions in this mode, the increase in the force constant of the Rh-Rh bond itself must be even greater.¹⁵ The large increase in the Rh-Rh stretching force constant clearly establishes that the Rh-Rh bond order is much higher in $E_u(^3A_{2u})$ than in $^1A_{1g}$, as predicted. An estimate of 42 kcal/mol for the Rh-Rh bond energy in $E_u(^3A_{2u})$ has been obtained⁹ from an analysis of the vibronic structure of the $E_u(^3A_{2u}) \leftarrow ^1A_{1g}$ system in the absorption spectrum of $\text{Rh}_2\text{b}_4^{2+}$. The 42 kcal/mol estimate is substantially larger than the 18 kcal/mol upper limit placed⁹ on the Rh-Rh bond energy in the ground state of $\text{Rh}_2\text{b}_4^{2+}$.

The Rh-Rh bond order will clearly decrease when $E_u(^3A_{2u})$ is quenched by electron transfer, whether the excited state gains an electron (in the $4d_{z^2}\sigma^*$ orbital) or loses an electron (from the $5p_z\sigma$ orbital). The Rh-Rh force constant change need not be the same, however, for reductive and oxidative quenching, because the $4d_{z^2}\sigma^*$ and $5p_z\sigma$ contributions to the force constant may differ considerably. These contributions are crucial because they control the Franck-Condon barriers associated with electron transfer to and from the $E_u(^3A_{2u})$ state as well as those for the electron back transfers of the Rh_2b_4^+ and $\text{Rh}_2\text{b}_4^{3+}$ product ions. Studies aimed at elucidating these points are in progress in our laboratories.

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(15) TR³ spectroscopic measurements on $\text{Rh}_2(\text{CNPh})_8^{2+}$ in CH_3CN solution yield 162 cm^{-1} for the Rh-Rh stretching frequency in the triplet state of this related unbridged complex. Here the increase in the Rh-Rh frequency over the ground-state value (60 cm^{-1}) is even more dramatic, apparently reflecting negligible mixing of ligand modes and the Rh-C deformation with the Rh-Rh stretching coordinate. The Rh-Rh force constant is roughly 7.3 times greater in $E_u(^3A_{2u})$ than in the ground state of $\text{Rh}_2(\text{CNPh})_8^{2+}$.

Thermal Desorption of Quaternary Ammonium Cations

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Quaternary ammonium salts are a challenge to the mass spectroscopist, both because they are difficult to analyze due to their nonvolatility and because a number of biologically important compounds (e.g., acetylcholine, choline chloride) are quaternary salts.¹ Attempts to volatilize quaternary ammonium salts prior to either electron ionization or chemical ionization (EI or CI) generally results in degradation to a neutral tertiary amine by loss of HX or RX (R = organic radical, X = halide). Ionization then produces R_3N^+ (EI) or R_3NH^+ (CI) and the appropriate fragments, from which the structure of the parent cation may be deduced.²

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