Deperturbation Analysis of the [18.5]1-X0$^+$ System and the Electronic Structure of ReN: A Laser Induced and Dispersed Fluorescence Study

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We report a deperturbation analysis of the [18.5]1-X0$^+$ system of ReN. Heterogeneous J_a uncoupling involving a "dark" ($\Omega = 2$) state is responsible for the observed perturbation. For the (0−0) band located near 540 nm, extra branches as well as an irregular energy level pattern are observed. For the (1−0) band near 510 nm, although the observed spectrum appears regular, the B′ value deduced from a previous analysis is not consistent with values associated with other vibrational levels. A careful reexamination of this band, using dispersed fluorescence to filter the laser induced fluorescence (LIF) spectra, allowed us to separate the "bright" and "dark" state contributions to the original LIF spectrum. In fact two spectra can be obtained, corresponding mainly either to the "bright" or to the "dark" excited states. Rotational analyses have been carried out for both of these (1−0) bands and confirm the deperturbation analysis of the (0−0) bands. Excited state lifetimes have been measured for individual ro-vibrational levels of the "bright" state. These lifetimes exhibit a large variation with rotational and vibrational quanta, an effect consistent with the proposed heterogeneous uncoupling mechanism. Dispersed fluorescence spectra have been recorded for all previously observed excited states. These spectra reveal the presence of a number of new low-lying states and the analysis helps to establish their Ω values. The current observations are consistent with the previously proposed electronic structure. However, the Franck−Condon factors inferred from the present study suggest that strong interactions exist among many of the excited states.

Introduction

Recently there has been a growing interest in gas phase spectroscopic studies of transition metal containing molecules, especially the simple diatomic metal−ligand molecules. The aims of these studies are to gain a general understanding of the electronic structure of these systems and to provide prototypical experimental calibrations for *ab initio* calculations. Rhenium metal, often alloyed with platinum, is used as a petroleum-reforming catalyst to produce low lead/high octane-rated gasoline,[1] and it has been observed that rhenium catalysts are exceptionally resistant to poisoning by nitrogen.[2]

One major problem, and thus the focus of the present research, is that the gas phase spectra frequently show perturbations due to interactions among the electronic states of the molecule. It is fair to say that the deperturbation analysis of a strongly perturbed spectrum offers both a challenge and enjoyment to molecular spectroscopic studies.[3] In general there are two classes of perturbations among electronic states: homogeneous perturbation between states with the same Ω values and heterogeneous perturbation between states with different Ω values. The coupling matrix elements for the former are independent of the rotational quantum number whereas for the latter they increase roughly linearly with J.[3−12]

Since the first gas phase spectroscopic study of the [23.8]1-X0$^+$ system[13] of ReN was reported,[14] transitions involving several other excited states of ReN have been observed.[15] One of these bands, with its origin around 540 nm, appears strongly perturbed (Figure 1): extra branches as well as an irregular energy level pattern are present.[16] We have undertaken several experimental approaches to "deperturb" the observed spectrum. These include measuring the excited state lifetimes, collecting dispersed fluorescence spectra, and separating the "bright" and "dark" state contributions to the LIF spectrum by monitoring the emissions with preselected wavelength windows. In this paper we present a detailed account of our deperturbation analysis and report on our current understanding about the electronic structure of the ReN molecule.

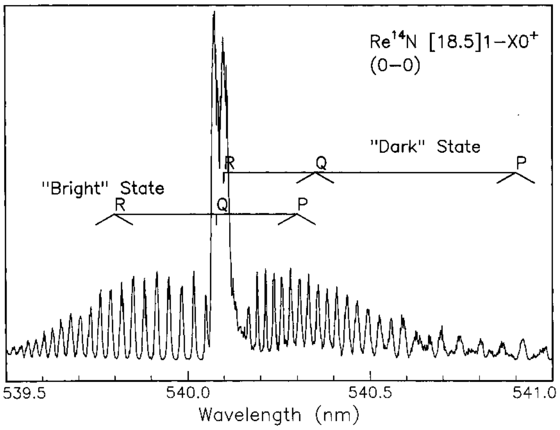

Figure 1. Perturbed ReN [18.5]1-X0$^+$ (0−0) band near 540 nm. The spectrum has two overlapping transitions involving interacting states. One transition is associated with the $\Omega' = 1$ "bright" state whereas the other is associated with a "dark" excited state.

Experimental Details

The experimental apparatus used in this study has been described previously.[15] Basically, the setup consists of a typical laser vaporization molecular beam source, two pulsed laser systems, and the data collecting and recording hardware and software for LIF detection.

A homemade pulsed molecular beam valve (pulse width = 200 μs, 0.5 mm diameter) was used with a rotating rhenium rod (5 mm diameter and 3 cm long, Johnson Matthey, 99.99%) mounted close to the opening of the nozzle. The second

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harmonic (532 nm) output of a Nd:YAG laser (Continuum NY60) was used as the vaporization source. Following every laser shot, the vaporized rhenium atoms/ions were expanded into the vacuum chamber with a mixture of carrier gases (2−5% ammonia in 1 atm of helium), through an attached 17 mm long (2 mm diameter) channel. Spectra of $Re^{15}N$ were obtained using $^{15}NH_3$ [Cambridge Isotopes, 98%]. The vacuum chamber, a 30 cm black anodized cubic aluminum one, was pumped by a 16 cm diffusion pump (Edwards Diffstack 160). Ion gauge readings of 1×10^{-4} and 1×10^{-5} Torr are typical with the molecular beam switched on and off, respectively.

A Nd:YAG pumped tunable dye laser (Lumonics HY600 and HD300) was used to excite the jet-cooled ReN molecules. A 0.2 cm^{-1} resolution was typical in the 375−540 nm region and several dyes (e.g., Exalite 376, 389, 404, and 416 and Coumarin 440, 460, 480, and 500) were used. The LIF detection system consists of a collection lens (50 mm diameter and $f = 75$ mm), a Jobin Yvon H20 monochromator (used as a band pass filter), and a photomultiplier tube (PMT; Hamamatsu R106UH). The signal from the PMT was collected on a digital oscilloscope (Tektronix 2440) and transferred to a 386 computer through an IEEE-488 interface. To record an LIF spectrum, the dye laser wavelength was scanned with a step size of 0.001nm, and for each wavelength setting, the signal was averaged for 10 laser shots. The LIF decay curves were also recorded at selected wavelengths by averaging the signals for 1000 laser shots.

The wavelength calibration of the dye laser was checked with the I_2 spectrum[17] near 500 nm and with the observed Re atomic LIF lines. The absolute wavenumbers reported here are believed to be accurate within 2 cm^{-1}, and the relative positions should be precise within 0.1 cm^{-1}.

In the low-resolution dispersed fluorescence experiment, the probe laser was fixed at selected wavelengths and the grating of the monochromator was rotated by using a stepping motor. Two 0.5 mm slits were used at the entrance and exit of the monochromator. The wavelength resolution of the monochromator is about 5 nm. The monochromator was calibrated by the excitation laser wavelength. The partial laser induced fluorescence spectra related to the “bright” and “dark” excited states were also recorded by parking the monochromator at selected wavelengths corresponding to the “bright” and “dark” state emissions, respectively.

To avoid power broadening and saturation in the strong [18.5]1-$X0^+$ transition, the amplifier of the dye laser was normally removed during our experiment. However, for the weak bands associated with “dark” states, the amplified dye laser output was used to enhance the signal.

Results and Analysis

The influence of perturbation is most clearly evident in the 540 nm band of $Re^{14}N$ (Figure 1), and in order to probe the nature of the interaction Hamiltonian, we recorded the corresponding $Re^{15}N$ spectrum in the same region. This $Re^{15}N$ spectrum is displayed in Figure 2a. It contains a small contribution from $Re^{14}N$, present as an impurity, which can readily be identified by direct comparison with the spectrum of pure $Re^{14}N$ (Figure 2b).

As may be seen from Figure 2 the two isotopic spectra differ much more than is to be anticipated from simply a difference in reduced mass. The effect of perturbation is much reduced in the $Re^{15}N$ isotopomer. The $Re^{14}N$ spectrum is relatively undegraded while the $Re^{15}N$ spectrum shows an R-head at a much lower J value, i.e., the upper state effective rotational constants (B) in the two species are quite significantly different. In addition, extra branches are observed in the $Re^{14}N$ spectrum which are not found for $Re^{15}N$.

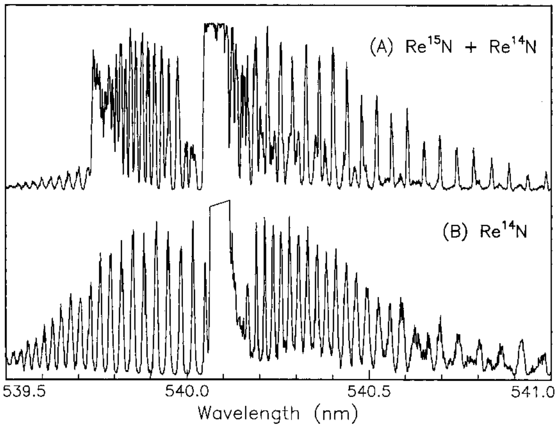

Figure 2. $Re^{15}N$ and $Re^{14}N$ [18.5]1-$X0^+$ (0−0) bands near 540 nm. Note that the effect of perturbation is significantly reduced in the $Re^{15}N$ spectrum.

TABLE 1: Spectroscopic Parameters (in cm^{-1}) of the Deperturbed $Re^{14}N$ [18.5]1 (v = 0, 1) and [18.5]2 (v = 0, 1) Levels[a]

state	T_e (±0.05)	B_e (±0.0003)	10^7D_e (±8)
[18.5]1 $v = 0$	18 509.6	0.4695	9
[18.5]1 $v = 1$	19 495.1	0.4649	7
[18.5]2 $v = 0$	18 505.8	0.4541	5
[18.5]2 $v = 1$	19 474.1	0.4501	0

[a] The values of the parameter p are 0.4412 and cm^{-1} 0.2181 cm^{-1}, for the $v = 0$ and $v = 1$ states, respectively.

We infer that the perturbation/interaction matrix elements must be small. The 540 nm band shows virtually no shift in position upon isotopic substitution, as is to be expected for a (0, 0) assignment. If the dominant perturbing level also has v' = 0, the interaction matrix elements must be of the order of a few cm^{-1} only. If the perturbing level has $v' = 1$, the interaction matrix elements should still be less than 100 cm^{-1}.

A deperturbation analysis was carried out on the $Re^{14}N$ band using the observed, strong and well-resolved R and P branch lines associated with the “bright” state, together with the weaker P branch lines associated with the “dark” state. The diagonal matrix elements of the two states were taken as $H_{11} = T_1 + B_1J'(J' + 1) - D_1[J'(J' + 1)]^2$ and $H_{22} = T_2 + B_2J'(J' + 1) - D_2[J'(J' + 1)]^2$.

Spin−orbit coupling for rhenium-containing molecules is expected to be quite strong [ζ(5d) for the Re atom is 2545 cm^{-1}], yet the observed interaction is weak. It therefore seemed unlikely that the coupling mechanism is homogeneous. Nevertheless we have carried out the deperturbation analysis using both the homogeneous and heterogeneous coupling matrix elements, as follows:[3]

homogeneous coupling, H_{12} = constant; heterogeneous coupling, $H_{12} = -p[J'(J' + 1) - \Omega_1\Omega_2]^{1/2}$ where $p = \langle\Psi_1|(J_{ax} + iJ_{ay})(2\mu r^2)^{-1}|\Psi_2\rangle$.

A satisfactory least-squares fit proved possible only with the heterogeneous perturbation. The spectroscopic constants obtained from this deperturbation analysis are listed in Table 1. The simulated spectrum based on these constants is compared with the experimental one in Figure 3. Several features are worth mentioning. First, in the simulation the f levels of the “bright” state (associated with the Q branch) are assumed perturbed in the same fashion as the e levels (associated with the P and R branches) in order to reproduce the appearance of the spectrum in the Q head region. Second, although rhenium

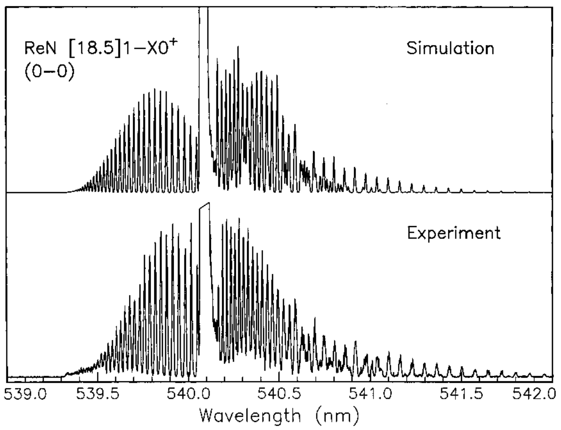

Figure 3. Experimental Re^{14}N [18.5]1-X0$^+$ (0−0) spectrum and a simulation based on our deperturbation analysis. In the simulation both *e* and *f* levels are assumed to be perturbed in an identical fashion. Any ^{185}ReN/^{187}ReN isotopic splitting is assumed negligible.

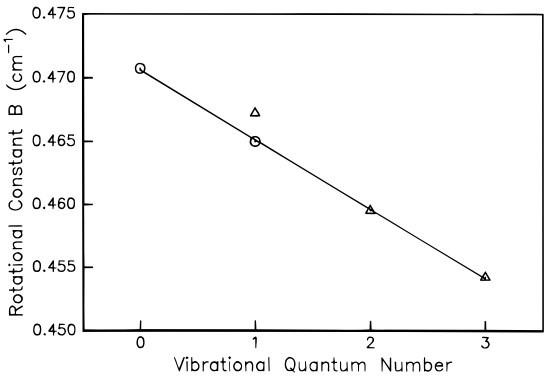

Figure 4. Excited state rotational constants of the [18.5]1-X0$^+$ system. Open circles represent values obtained from our deperturbation analysis whereas the open triangles plotted are based on our previous analysis.

has two naturally-occurring isotopes, ^{185}Re (37.4%) and ^{187}Re (62.6%), lines due to ^{185}ReN and ^{187}ReN molecules are not resolved in the experimental P-branch spectrum associated with the "dark" levels. We take this as an indication that the perturbing state most probably has $v' = 0$. The ^{185}ReN/^{187}ReN isotopic splitting for any 1−0 bands we have examined is typically of the order of 0.4 cm^{-1} and well resolved. Third, as may be seen by comparing the respective baselines for the R- and P-branch regions associated with the "bright" state in the experimental spectrum (Figure 3), the P-branch contains an underlying background. Our simulation suggests that this background comes from Q-branch structure of the transition to the "dark" state.

In Figure 4, the *B* value of the deperturbed $v' = 0$ "bright" state is compared with *B* values from higher vibrational levels of the same electronic state, obtained from our earlier study.[15,16] It is evident from the graph that the deperturbed *B* value for $v' = 0$ is in line with B values of the other vibrational levels, with the exception of $v' = 1$. The obvious conclusion is that the spectrum associated with the $v' = 1$ level of the [18.5]1 state also suffers somewhat from the perturbation, and additional experiments have been carried out to explore this possibility. The LIF spectrum of the (1, 0) [18.5]1-X0$^+$ transition of Re^{14}N was re-examined. Emissions to different lower states were wavelength filtered to separate as much as possible the contributions to the total LIF spectrum from the "bright" and "dark" states. The results are shown in Figure 5. The LIF spectrum in Figure 5b is associated with the "bright" state and is almost free of any contribution from the "dark" state. In Figure 5c the dominant contribution is from the "dark" state, although one can also observe lines associated with the high *J* levels of the "bright" state. Attempts to achieve a similar degree of separation for the (0, 0) band proved less successful because the $v = 0$ mixing is more severe.

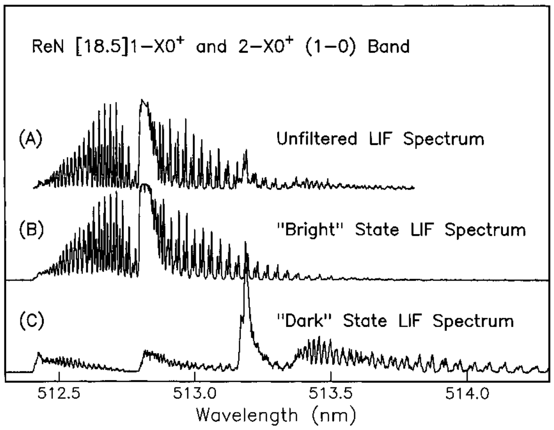

Figure 5. LIF spectra associated with the [18.5]1-X0$^+$ and [18.5]2-X0$^+$ transitions. In (A) the LIF spectrum was recorded with emissions to all lower states (i.e., with no wavelength filtering) whereas in (B) and (C) the emission to different lower states was monitored to separate the LIF spectra associated with the "bright" and "dark" states, respectively. Spectrum B was recorded with the monochromator centered at 518 nm whereas, for spectrum C, a wavelength of 690 nm was used.

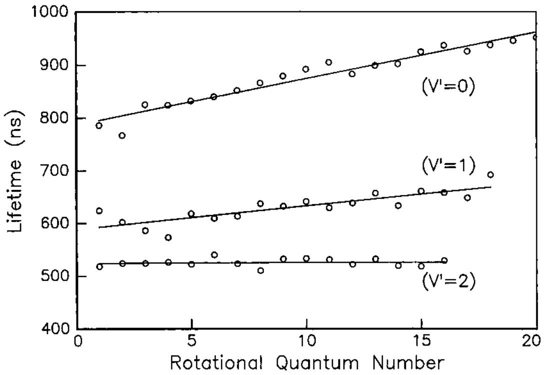

Figure 6. Excited state lifetimes for the "bright" states. The strong *J* dependence is consistent with the *J*-dependent heterogeneous coupling. The lifetimes have not been corrected for any wavelength dependence or for any *r* dependence in the transition moment function. Such effects are expected to be small.

A deperturbation analysis of the two (1−0) bands has been carried out, and the resulting spectroscopic constants were found to agree with the findings in the (0, 0) analysis. The $v' = 1$ parameters are also included in Table 1. The magnitude of the p parameter, for both $v' = 1$ and $v' = 0$ states, is comparable to the rotational constant of ReN. This is expected from the nature of the heterogeneous perturbation.[3]

In order to confirm further the proposed *J*-dependent heterogeneous coupling we made measurements of excited state lifetimes in the $v' = 0$, 1, and 2 levels of the "bright" ($\Omega = 1$) state. These measurements are graphed in Figure 6. The results indicate a strong dependence of the lifetime on the vibrational quantum number and, for $v' = 0$ and 1, a significant dependence on rotational quantum number. The rotational dependence is more pronounced for the $v = 0$ level. Such a rotational dependence is as expected from heterogeneous coupling, whereas the vibrational dependence may be indicative of additional homogeneous coupling to other states.[18]

In our earlier study[15] we proposed an electronic structure for ReN based upon experimental observations, molecular orbital considerations, and *ab initio* calculations on related metal−

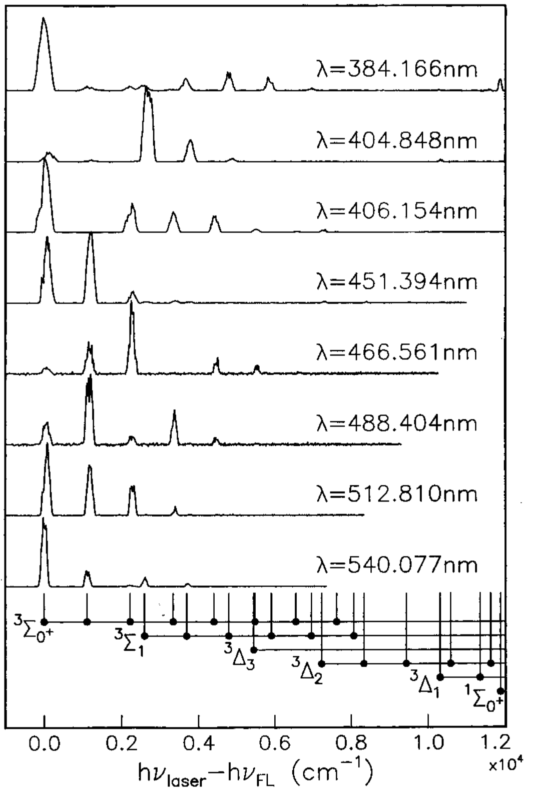

Figure 7. Representative dispersed fluorescence spectra of Re^{14}N.

nitrogen diatomic systems. The presence of several (unobserved) low-lying electronic states could be inferred from the proposed structure. We have now found direct evidence from dispersed fluorescence experiments for five low-lying electronic states in addition to the ground state. The dispersed fluorescence spectra were recorded for all but one of the previously observed excited states. Examples of these spectra are shown in Figure 7. The Franck−Condon factors inferred from these dispersed fluorescence spectra are highly sensitive to the excited state involved. This effect can only be understood if the upper or lower state is strongly mixed with other electronic states having very different *B* values.

We have constructed an energy level diagram of the various electronic states of ReN, including the new low-lying states observed in the present study. This term diagram is shown in Figure 8 which includes all observed transitions. Specific data relating to the low-lying states are listed in Table 2.

Discussion

A. The Nature of the Perturbing “Dark” State. When heterogeneous perturbation is involved, the perturbing “dark” state must have an Ω value different from that of the perturbed “bright” state. Given that the “bright” state has an $\Omega = 1$, the possible values of Ω for the “dark” state are 0 and 2. The observation that both *e* and *f* levels are perturbed in an identical fashion eliminates the possibility of $\Omega = 0$, since a state with $\Omega = 0$ has only one set of rotational levels (*e* for 0^+ and *f* for 0^- state) and only half of the “bright” ($\Omega = 1$) levels would be perturbed. The heterogeneous couplings are associated with the rotational part of the Hamiltonian and fall into three cases:[3] (i) S-uncoupling, where the two interacting states have identical *S* and Λ quantum numbers but differ in their value of Σ; (ii) *L*-uncoupling, where the two states have identical *S* and Σ but differ in their value of Λ; and (iii) J_a uncoupling, where both states belong to Hund’s case (c) and Λ, Σ, and *S* are no longer good quantum numbers.

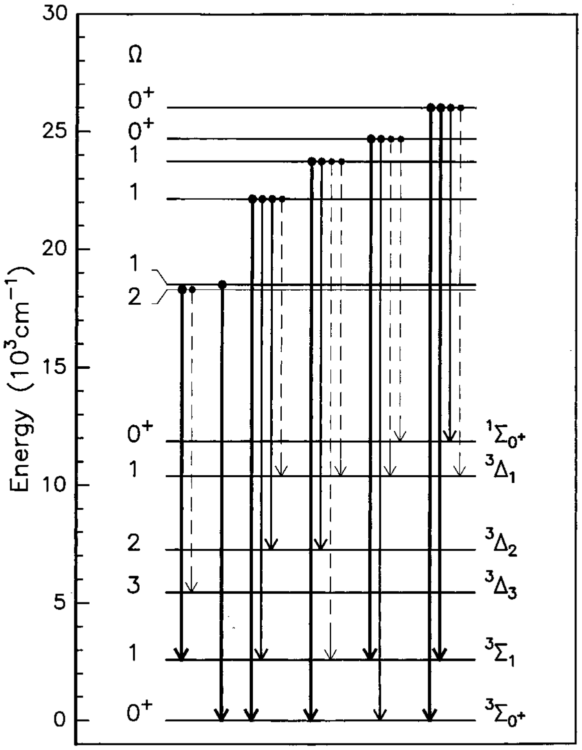

Figure 8. Observed emissions and electronic states of ReN. Refer to the text for the assignment of these states. Thick lines indicate strong emissions, thin lines represent weak emissions, and dashed lines stand for very weak emissions.

TABLE 2: Term Values and Vibrational Constants (in cm^{-1}) of Low-Lying Electronic States of Re^{14}N

designation	Ω	T$_e$ (±100)	ω_e (±50)
X$^3\Sigma^-_0$	0^+	0	1080
$^3\Sigma^-_1$	1	2 630	1100
$^3\Delta_3$	3	5 450	*a*
$^3\Delta_2$	2	7 260	1050
$^3\Delta_1$	1	10 340	1040
$^1\Sigma^+_0$	0^+	11 870	*a*

[a] Only one vibrational level was observed for these states.

Our deperturbation analysis indicates that the interacting “bright” and “dark” states have significantly different *B* values. Spin−orbit interaction in rhenium-containing molecules is expected to be strong [$\zeta(5d) = 2545$ cm^{-1}][3] and there should be a marked tendency toward case c. It is evident that there are several excited states with $\Omega = 1$ and 0 close to the interacting “bright” and “dark” states. In light of these observations the most probable situation in ReN is that of two case c states interacting via the J_a uncoupling operator.

B. Electron Configurations and Symmetries of the Low-Lying States. We have already published evidence[15] in support of a $^3\Sigma^-{}_0$ ground state for ReN derived from the electron configuration $\delta^2\sigma^2$. Other states, expected to be low-lying, arise from this same configuration and other configurations. While there are strong mixings and a tendency toward case c in the higher excited states ($T > 15\,000$ cm^{-1}), this may not be as true for the lower states. If the density of states of the same Ω in the region up to 12 000 cm^{-1} is not too high, and spin−orbit coupling can still be viewed as a perturbation, a state designation in terms of case a parentage may be useful. However, case c selection rules, $\Delta\Omega = 0$ and ±1, are expected for all transitions to and from the strongly mixed case c excited states. All of the low-lying states with $\Omega = 0-3$ should be connected to at least one of the observed upper states. We have been able to establish the Ω values for all of the newly observed low-lying electronic states, and these assignments are included in Figure 8.

The first excited state has $T \approx 2500$ cm^{-1} and is connected to upper levels with $\Omega = 0$, 1, and 2. Following case c selection rules it must then have $\Omega = 1$. The second excited state has $T \approx 6000$ cm^{-1} and is connected very weakly to only the "dark" $\Omega = 2$ state. We infer its Ω value must be 3. The assignment of the case a parentage states associated with the observed low-lying states was then established on the basis of spin−orbit interaction and the known location of the states. The picture which emerges from this study in terms of an energy level pattern and associated case a parentage states is consistent with expectations from $\delta^2\sigma^2$ and $\delta^3\sigma^1$ electron configurations and the spin−orbit coupling constant for Re.

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(18) Note that heterogeneous perturbations should have only minimal effect on low *J* levels. The observed lifetime changes at low *J* can therefore be related only to homogeneous perturbations.