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# High-Resolution Infrared Spectrum of the $\nu_1$ Band of $\eta^5$-$C_5H_5NiNO$

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Gas-phase rotational constants and distortion constants have been determined for the $\nu_1$ ($v = 1$) excited vibrational state of cyclopentadienylnickel nitrosyl ($C_5H_5NiNO$) using a high-resolution Fourier transform spectrometer system at Kitt Peak, Arizona. The rotationally resolved lines have been measured for the C−H symmetric stretch vibration ($\nu_1 = 3110$ cm$^{-1}$). In the present analysis, over 150 lines have been assigned and fitted using a rigid-rotor Hamiltonian with centrifugal distortion. The vibrational band center, excited-state rotational constants, and distortion constants derived from the measured spectrum for this prolate symmetric-top molecule are $\nu_o = 3110.4129(4)$ cm$^{-1}$, $A' = 0.14328(8)$ cm$^{-1}$, $B' = C' = 0.041285(1)$ cm$^{-1}$, $D_{J'} = 0.078(1)$ kHz, $D_{JK'} = 2.23(4)$ kHz, and $D_{K'} = -2.63(2)$ kHz, respectively. Several different combination differences, with a common upper state, were calculated for different $K$ stacks for the observed spectra, and the consistency of the lower state rotational constants obtained provided further support for the current assignment. The ground-state rotational constant ($B''$) derived from this combination differences analysis agrees with the previously obtained Fourier transform microwave value to within 0.15%. However, ground-state rotational constants, $A''$ and $B''$, have been fixed in the present analysis to avoid correlation effects and to get more accurate results. The new measured parameters are compared with the previously obtained results from Fourier transform microwave and infrared spectroscopy measurements. The C−H vibration stretching frequency and rotational constants were calculated using density functional theory calculations, and these were quite helpful in resolving ambiguities in the fitting procedure and for initial assignments of measured lines.

## Introduction

There has been a considerable amount of interest in $\pi$-bonded organometallic transition metal complexes since the initial discovery and characterization of ferrocene.[1,2] These $\pi$-bonded transition metal complexes have played an important role in the development of organometallic chemistry. The complex, cyclopentadienylnickel nitrosyl (CpNiNO) appears to be one of the first organometallic complexes to be studied using microwave spectroscopy.[3] This complex (CpNiNO) has been found to be an excellent catalyst for cyclo-oligomerization of dialkenes[4,5] and polymerization of terminal alkynes.[6]

Studies using various different isotopic species have revealed that this complex has a linear Ni−N−O system and a five-fold axis of symmetry ($C_5$) orthogonal to the $C_5H_5$ plane.[7,8] The $C_{5v}$ symmetry axis was established by the correlation of line intensities with the calculated nuclear spin statistics of the molecule. Even though an earlier electron diffraction study[9] had suggested a bent Ni−N−O system, Ronova and co-workers[10] later showed that the Ni−N−O moiety is linear and that the structure is consistent with the gas-phase microwave structure. The nuclear quadrupole coupling constant for $^{14}$N ($I = 1$) has been determined using Fourier transform microwave spectroscopy (FTMW) by two groups.[11,12] The analyses using two different models (Townes−Daily model[11] and Pauling model[12]) indicate that the Ni−N bond exhibits primarily double-bond character.

Several research groups have studied low-resolution infrared spectra of this complex in different phases to assign various infrared and Raman active frequencies.[13−16] Moreover, photoelectron studies[17,18] have yielded orbital energies and ionization energies of the CpNiNO complex.

In the present work, the high-resolution infrared spectrum of CpNiNO has been recorded in the frequency range of 2500−5700 cm$^{-1}$. The symmetric-top structure of CpNiNO has made it easier to analyze this high-resolution infrared data. There are 33 fundamental vibrational modes of CpNiNO, which can be described with their symmetry and activity as follows; six $A_1$-IR active/Raman depolarized, one $A_2$-IR/Raman inactive, seven $E_1$-IR active/Raman depolarized, and six $E_2$-Raman depolarized, where the $A_1$, $A_2$ and $E_1$, $E_2$ modes are singly and doubly degenerate,[13] respectively. In the present analysis, the rovibrational spectrum for the $A_1$ symmetric C−H stretch ($\nu_1$ vibrational mode) has been analyzed using a Fourier transform spectrometer (FTS) system available at Kitt Peak Arizona. For the $\nu_1$ stretch mode, the transition dipole moment lies along the main symmetry axis (see Figure 1), so this gives rise to a parallel (//) type band. Various different researchers have measured this $\nu_1$ symmetric stretch to be between 3110 and 3118 cm$^{-1}$ for different phases. However, the report of a detailed infrared analysis in the gas phase by Feltham and co-workers[13] located the $\nu_1$ C−H stretch at 3110 cm$^{-1}$.

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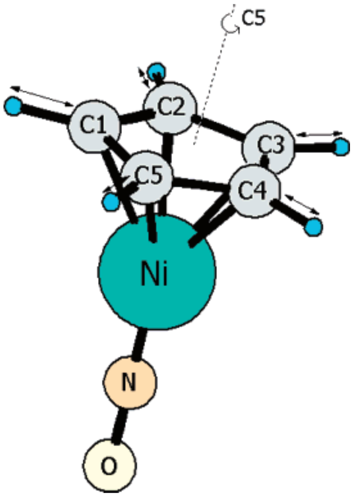

**Figure 1.** Molecular structure of cyclopentadienylnickel nitrosyl; the CpNiNO obtained from the DFT calculations is shown. The symmetric C−H bond stretching for the $\nu_1$ mode and the $C_5$ symmetry axis are also illustrated.

**TABLE 1: Experimental Parameters and Settings for the FT Spectrometer**

| | |
|---|---|
| spectral coverage | 1780−5700 cm$^{-1}$ |
| resolution used (fwhm) | 0.006 cm$^{-1}$ |
| number of coadded scans | 10 |
| recording time | ∼1 h |
| absorbing path length | 1.38 m |
| aperture diameter | 3.0 mm |
| source | quartz halogen |
| beam splitter | KCl |
| detectors (2) | InSb |
| optical filters | wedged Ge |

The present work has yielded rotational constants and distortion constants for the upper vibrational state, in addition to a more precise value for the $\nu_1$ symmetric stretching vibrational mode. A comparison is made between theoretical calculations and the present, new, high resolution infrared data, and this is expected to aid in understanding the structure of this molecule in the vibrational excited state.

## Experiment

The preparation of the CpNiNO sample was based on a published synthesis procedure by Piper et al.[19] In a typical synthesis, a suspension containing dicyclopentadienyl nickel (nickelocene) in dry *n*-pentane was prepared inside a dry box. This was capped with a rubber septum, and NO gas was passed through this suspension for several hours with constant stirring while keeping the reaction mixture at ice temperature. The resulting red color solution, in the presence of sludge, was vacuum distilled with a short distillation arm to obtain the title compound, CpNiNO, as a bright red liquid. The product was isolated in a small round-bottom flask at dry ice temperature. The CpNiNO complex has about 10 Torr of vapor pressure at room temperature, and this is sufficient for gas-phase IR spectroscopy.

The vibration−rotation spectra were recorded using a 1 m FTS located at the McMath−Pierce facility of the National Observatory (NSO) at Kitt Peak, Arizona. The basic experimental details and experimental setup are given in Table 1.

To collect the absorption spectra of CpNiNO, a cylindrical glass sample cell (1.38 m long) was placed between the infrared source and the entrance aperture of the FTS, with the ends of the sample cell capped with $CaF_2$ windows having O-ring seals. This sample cell was constructed with a valve at one end to admit the sample. A T-joint was attached to this adjustable valve, and one end was connected to two liquid nitrogen-cooled traps followed by a vacuum pump. A small glass sample cell, with another valve containing CpNiNO, was attached to the other end of this T-joint to introduce the CpNiNO vapor. The absolute accuracy of the instrument was 0.056 cm$^{-1}$, based on calibrations using a HeNe single-frequency reference laser and measuring near-infrared acetylene lines, with well-known frequencies. Quick scans were taken at different concentrations and pressures of CpNiNO before finding the “best” set of conditions. Once optimized, the spectra were recorded with the basic set up parameters (see Table 1). Before introducing the sample of CpNiNO to the main sample cell tube, a high-resolution spectrum of the empty cell was recorded under the same basic experimental conditions to allow subtraction of a background. All of the spectra were recorded at room temperature. A sample spectrum in the 3040−3058 cm$^{-1}$ region is shown in Figure 2.

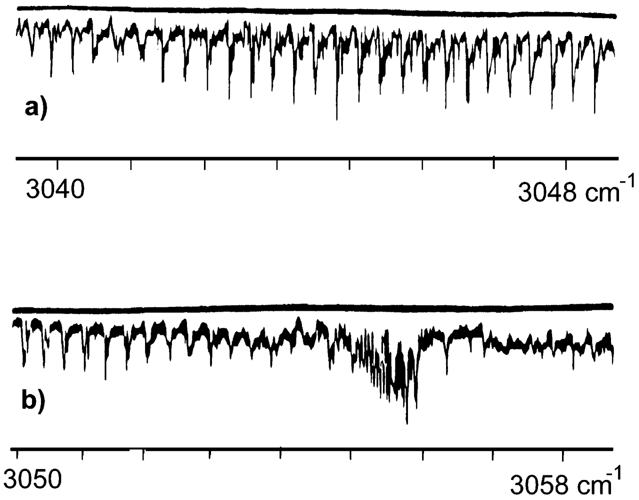

**Figure 2.** Example spectrum for the 3040−3058 cm$^{-1}$ region, showing (a) reasonably well-resolved transitions and (b) Q-branch transitions near 3056 cm$^{-1}$, which are not resolved.

## Results

**Theory.** Different theoretical methods and basis sets were tested in the quest to find the best calculated structure for CpNiNO. The final method used was density functional theory (DFT) with Becke’s three-parameter functional with the nonlocal correlation provided by Perdew and Wang (B3PW91).[20−22] The following basis sets were used to compare the structural results: (i) Los Alamos double-ζ basis set, (LANL2DZ);[23−25] (ii) Dunning/Huzinaga valence double-ζ on carbon, nitrogen, oxygen, and hydrogen atoms with Stuttgart/Dredsen electron core potentials on nickel atom (SDD); and[7,26] (iii) Hay−Wadt ($n + 1$) basis set with effective core potential for nickel[27] and split-valence plus polarization basis set (SVP)[28,29] for carbon, nitrogen, oxygen, and hydrogen atoms.

All geometry optimization methods were followed by a frequency analysis to ensure that the stationary points found were at least local minima. The B3PW91 calculations with different basis sets predict structural parameters and rotational constants closer to the experimental values. These calculations were performed using the options vibrot and anharmonic. These options may be used along with the optimization and frequency routines in Gaussian 03 to calculate zero-point energies, anharmonic frequencies, and anharmonic vibration−rotation couplings.[30−33]

Results from the theoretical calculations, using the options vibrot and anharmonic, were used to aid the assignments of quantum numbers for the various transitions. These calculations not only predict the rotational constants for the equilibrium ($r_e$) structure of the molecule but also predict the constants for the ground ($r_0$) and the excited vibrational states for the molecule.

We found that the preferred method and the basis set used to predict the geometry and the structure of CpNiNO is B3PW91 with the Hay−Wadt ($n + 1$) basis set and an effective core potential for nickel and the SVP for the carbon, nitrogen, oxygen, and hydrogen atoms. This method and the basis set combination were preferred because the harmonic frequencies of the molecule were closer to the experimental gas-phase low-resolution infrared spectrum values for the molecule, after scaling the theoretical values with a standard correction factor of 0.9607.[34] The second reason for preferring this method and basis set is that the rotational constant, $B$ ($=C$) for the $r_0$ structure was closer to the measured value from the gas-phase FTMW spectroscopy measurements.[11] All of the calculated values are given in Table 3 along with the respective current and previous experimental values.

All of the theoretical calculations were performed an on HP/Compaq Alpha supercomputer (AURA) using Gaussian-03 Programs,[35] which is available at the University of Arizona.

**Data Analysis.** Line lists for the center frequencies for the observed transitions were generated for this complex using the software PC-GREMLIN. As part of the process of selecting the transitions for the CpNiNO molecule, the measured spectrum was ratioed to the empty cell spectrum recorded under the same experimental conditions. This spectrum was used for the analysis using PC-GREMLIN. To double check, the transitions could be correctly attributed to be the CpNiNO complex; the line frequencies were cross-checked with the Hitran[36] database for all other listed molecules in the infrared frequency range of interest (3110−3120 cm$^{-1}$).

All of the assigned transitions for CpNiNO, which were used in the fit, are listed in Table 2. Out of many lines observed (close to 1500), 155 lines were carefully selected to be used in the fitting program, SPFIT,[37] which employs a standard rigid-rotor Hamiltonian with centrifugal distortion.[38] Because the uncertainties for derived parameters are normally underestimated when using SPFIT, a program, PIFORM,[39] was used to correct the fitted parameter uncertainties to obtain values of the various constants with conventional standard errors.

Transitions obtained for the prolate symmetric top, CpNiNO, were fitted using six adjustable parameters, namely, (i) rotational constants for the excited vibrational state ($A'$, $B'$), (ii) centrifugal distortion constants for the excited state ($D_{J'}$, $D_{JK'}$, and $D_{K'}$), and (iii) pure vibrational frequency (the energy difference between $v = 0$ and $v = 1$ level) for the $\nu_1$ mode. In the fitting analysis, the ground-state rotational constants ($A''$, $B''$) and the distortion constants ($D_{J''}$, $D_{JK''}$, and $D_{K''}$) were held fixed to the previously obtained more precise values from FTMW measurements[11] and the current DFT values. In addition, effects of the nuclear quadrupole coupling due to $^{14}N$ were ignored as the splitting due to N nuclear quadrupole interaction is much smaller than the resolution of the FTS instrument (0.006 cm$^{-1}$). The fitted parameters from the least-squares fit along with the calculated values and previous experimental values are presented in Table 3 for comparison.

The first fundamental vibrational band corresponding to the $A_1$ symmetric stretch of C−H has been analyzed. As mentioned above, this band is due to the transition dipole moment parallel to the $z$-axis (symmetry axis) and gives an IR-active, parallel (//) band. Therefore, the transitions obey the parallel selection rules $\Delta K = 0$ with $\Delta J = \pm 1$ for the $K' = 0 \leftarrow K'' = 0$ transition and $\Delta J = 0, \pm 1$ transitions for $K \neq 0$. The intensities of these lines are governed by the Hönl−London factors.[40] The energy expression used for the $Q$-branch transitions is shown in eq 1 below.[40] Note that the distortion constants are not included in this equation, but symmetric-top quartic distortion constants ($D_J$, $D_{JK}$, and $D_K$) were included in the fitting procedure.

$$\nu_o^{\mathrm{sub}} = \nu_o + [(A_{[v]}' - A_{[v]}'') - (B_{[v]}' - B_{[v]}'')]K^2 \qquad (1)$$

In eq 1, $A'$ and $B'$ represent the rotational constants for the upper vibrational state and $A''$ and $B''$ are the rotational constants for the ground vibrational state. The whole parallel band will appear to consist of one $P$-, one $R$-, and the blended-line $Q$-branch. Each of these lines consists of a number of components ($J + 1$ in the $R$-branch and $J$ in the $P$-branch). This $PQR$-branch structure was readily observed in the current spectra indicating that this molecule is symmetric top. Altogether, 88 $P$-branch transitions and 67 $R$-branch lines for various $K$-stacks were fitted in the current analysis with a standard deviation of 0.0022 cm$^{-1}$ (see Table 2). However, no $Q$-branch transitions were well-resolved and hence were not included in the current analysis. The equations for the $P$- ($\Delta J = -1$) and the $R$- ($\Delta J = +1$) branches are similar to eq 1, except for the additional terms, which are $B'[(J + 1)(J + 2)] - B''[J(J + 1)]$ for the $R$-branch and $B'[(J - 1)J] - B''[J(J + 1)]$ for the $P$-branch.

## Discussion

The high-resolution infrared spectrum of the $\nu_1$ band of the $\pi$-bonded transition metal complex, CpNiNO, has been measured and analyzed. The analysis yields the rotational constants ($A'$, $B'$ ) for the vibrational excited state, distortion constants for the excited state, and the fundamental $\nu_1$ C−H stretching frequency for the CpNiNO molecule. The reported values agree well with the previously measured experimental and calculated values (see Table 3) to within the experimental uncertainties. A convincing set of combination differences involving a common upper level (LSCD) have been calculated for several different transitions for various different $K$-stacks. These calculations yielded lower state rotational constants ($B''$) and as can be seen in Table 4; the consistency of the values obtained for $B''$ further supports the validity of the current assignment and the fit results. These combination differences have been calculated with respect to seven different, common upper rotational states (see Table 4). However, the deviations in the ground rotational constants from this analysis are about 2 MHz when compared to the previously obtained FTMW value.[11] Nevertheless, this level of agreement is as good as we would expect considering the experimental errors for the measured IR lines. The ground-state rotational constants, $A''$ and $B''$, along with the ground-state distortion constants were held fixed to the FTMW results in the current analysis to obtain more reliable parameters for the excited state. The present study also provided the fundamental C−H stretching frequency, 3110.4129(4) cm$^{-1}$, and we believe that this value is much more accurate than the previous low-resolution infrared value obtained by Feltham and co-workers.[13]

The rotational constants, $A'$ and $B'$, obtained for the upper vibrational state from the present study are 0.14328(8) and 0.041285(1) cm$^{-1}$. Furthermore, the excited-state rotational constant $B'$ obtained experimentally is 0.00072 cm$^{-1}$ lower than

**TABLE 2: Measured and Calculated Vibration−Rotation Transition Frequencies for CpNiNO and the Fit Residuals (M−C)[a]**

| $J'$ | $K'$ | $v'$ | $J''$ | $K''$ | $v''$ | measured | calculated | M−C |
|---|---|---|---|---|---|---|---|---|
| 45 | 0 | 1 | 46 | 0 | 0 | 3105.2096 | 3105.2093 | 0.0004 |
| 45 | 1 | 1 | 46 | 1 | 0 | 3105.2069 | 3105.2073 | −0.0004 |
| 45 | 2 | 1 | 46 | 2 | 0 | 3105.2020 | 3105.2016 | 0.0005 |
| 45 | 3 | 1 | 46 | 3 | 0 | 3105.1920 | 3105.1920 | 0.0000 |
| 44 | 2 | 1 | 45 | 2 | 0 | 3105.3439 | 3105.3442 | −0.0003 |
| 44 | 1 | 1 | 45 | 1 | 0 | 3105.3502 | 3105.3500 | 0.0003 |
| 44 | 0 | 1 | 45 | 0 | 0 | 3105.3510 | 3105.3519 | −0.0009 |
| 43 | 1 | 1 | 44 | 1 | 0 | 3105.4915 | 3105.4913 | 0.0002 |
| 43 | 0 | 1 | 44 | 0 | 0 | 3105.4932 | 3105.4932 | 0.0000 |
| 42 | 5 | 1 | 43 | 5 | 0 | 3105.5870 | 3105.5869 | 0.0001 |
| 42 | 4 | 1 | 43 | 4 | 0 | 3105.6035 | 3105.6032 | 0.0003 |
| 42 | 3 | 1 | 43 | 3 | 0 | 3105.6159 | 3105.6162 | −0.0003 |
| 42 | 2 | 1 | 43 | 2 | 0 | 3105.6252 | 3105.6256 | −0.0004 |
| 42 | 1 | 1 | 43 | 1 | 0 | 3105.6310 | 3105.6312 | −0.0002 |
| 42 | 0 | 1 | 43 | 0 | 0 | 3105.6232 | 3105.6331 | −0.0099 |
| 41 | 1 | 1 | 42 | 1 | 0 | 3105.7701 | 3105.7699 | 0.0002 |
| 41 | 0 | 1 | 42 | 0 | 0 | 3105.7720 | 3105.7718 | 0.0002 |
| 40 | 4 | 1 | 41 | 4 | 0 | 3105.8802 | 3105.8795 | 0.0007 |
| 40 | 3 | 1 | 41 | 3 | 0 | 3105.8922 | 3105.8923 | −0.0001 |
| 40 | 2 | 1 | 41 | 2 | 0 | 3105.9012 | 3105.9016 | −0.0004 |
| 40 | 1 | 1 | 41 | 1 | 0 | 3105.9067 | 3105.9072 | −0.0005 |
| 40 | 0 | 1 | 41 | 0 | 0 | 3105.9131 | 3105.9091 | 0.0040 |
| 39 | 4 | 1 | 40 | 4 | 0 | 3106.0162 | 3106.0156 | 0.0006 |
| 39 | 3 | 1 | 40 | 3 | 0 | 3106.0289 | 3106.0284 | 0.0005 |
| 39 | 2 | 1 | 40 | 2 | 0 | 3106.0371 | 3106.0376 | −0.0005 |
| 39 | 1 | 1 | 40 | 1 | 0 | 3106.0425 | 3106.0432 | −0.0007 |
| 39 | 0 | 1 | 40 | 0 | 0 | 3106.0569 | 3106.0451 | 0.0118 |
| 38 | 4 | 1 | 39 | 4 | 0 | 3106.1468 | 3106.1504 | −0.0036 |
| 38 | 3 | 1 | 39 | 3 | 0 | 3106.1635 | 3106.1631 | 0.0004 |
| 38 | 2 | 1 | 39 | 2 | 0 | 3106.1719 | 3106.1723 | −0.0004 |
| 38 | 1 | 1 | 39 | 1 | 0 | 3106.1778 | 3106.1779 | −0.0001 |
| 38 | 0 | 1 | 39 | 0 | 0 | 3106.1776 | 3106.1798 | −0.0022 |
| 37 | 2 | 1 | 38 | 2 | 0 | 3106.3049 | 3106.3057 | −0.0008 |
| 37 | 1 | 1 | 38 | 1 | 0 | 3106.3155 | 3106.3113 | 0.0042 |
| 37 | 0 | 1 | 38 | 0 | 0 | 3106.3148 | 3106.3132 | 0.0016 |
| 36 | 3 | 1 | 37 | 3 | 0 | 3106.4266 | 3106.4287 | −0.0021 |
| 36 | 2 | 1 | 37 | 2 | 0 | 3106.4384 | 3106.4378 | 0.0006 |
| 36 | 1 | 1 | 37 | 1 | 0 | 3106.4435 | 3106.4434 | 0.0002 |
| 36 | 0 | 1 | 37 | 0 | 0 | 3106.4451 | 3106.4452 | −0.0001 |
| 33 | 1 | 1 | 34 | 1 | 0 | 3106.8319 | 3106.8316 | 0.0003 |
| 33 | 0 | 1 | 34 | 0 | 0 | 3106.8379 | 3106.8335 | 0.0045 |
| 31 | 7 | 1 | 32 | 7 | 0 | 3106.9978 | 3107.0016 | −0.0038 |
| 31 | 5 | 1 | 32 | 5 | 0 | 3107.0399 | 3107.0415 | −0.0016 |
| 31 | 4 | 1 | 32 | 4 | 0 | 3107.0560 | 3107.0571 | −0.0011 |
| 31 | 3 | 1 | 32 | 3 | 0 | 3107.0680 | 3107.0695 | −0.0015 |
| 31 | 2 | 1 | 32 | 2 | 0 | 3107.0765 | 3107.0784 | −0.0019 |
| 31 | 1 | 1 | 32 | 1 | 0 | 3107.0840 | 3107.0839 | 0.0001 |
| 31 | 0 | 1 | 32 | 0 | 0 | 3107.0850 | 3107.0857 | −0.0007 |
| 29 | 1 | 1 | 30 | 1 | 0 | 3107.3315 | 3107.3309 | 0.0006 |
| 29 | 0 | 1 | 30 | 0 | 0 | 3107.3335 | 3107.3327 | 0.0008 |
| 26 | 7 | 1 | 27 | 7 | 0 | 3107.6074 | 3107.6107 | −0.0033 |
| 26 | 6 | 1 | 27 | 6 | 0 | 3107.6475 | 3107.6316 | 0.0159 |
| 26 | 5 | 1 | 27 | 5 | 0 | 3107.6493 | 3107.6499 | −0.0006 |
| 26 | 4 | 1 | 27 | 4 | 0 | 3107.6641 | 3107.6652 | −0.0011 |
| 26 | 3 | 1 | 27 | 3 | 0 | 3107.6765 | 3107.6774 | −0.0009 |
| 26 | 2 | 1 | 27 | 2 | 0 | 3107.6858 | 3107.6863 | −0.0005 |
| 26 | 1 | 1 | 27 | 1 | 0 | 3107.6908 | 3107.6916 | −0.0008 |
| 26 | 0 | 1 | 27 | 0 | 0 | 3107.6924 | 3107.6934 | −0.0010 |
| 24 | 2 | 1 | 25 | 2 | 0 | 3107.9192 | 3107.9203 | −0.0011 |
| 24 | 1 | 1 | 25 | 1 | 0 | 3107.9243 | 3107.9256 | −0.0013 |
| 24 | 0 | 1 | 25 | 0 | 0 | 3107.9253 | 3107.9274 | −0.0021 |
| 22 | 1 | 1 | 23 | 1 | 0 | 3108.1538 | 3108.1543 | −0.0005 |
| 22 | 0 | 1 | 23 | 0 | 0 | 3108.1555 | 3108.1561 | −0.0006 |
| 19 | 2 | 1 | 20 | 2 | 0 | 3108.4816 | 3108.4824 | −0.0008 |
| 19 | 1 | 1 | 20 | 1 | 0 | 3108.4882 | 3108.4876 | 0.0006 |
| 19 | 0 | 1 | 20 | 0 | 0 | 3108.4826 | 3108.4894 | −0.0068 |
| 16 | 4 | 1 | 17 | 4 | 0 | 3108.7821 | 3108.7834 | −0.0013 |
| 16 | 3 | 1 | 17 | 3 | 0 | 3108.7948 | 3108.7953 | −0.0005 |
| 16 | 2 | 1 | 17 | 2 | 0 | 3108.8036 | 3108.8040 | −0.0004 |
| 11 | 1 | 1 | 12 | 1 | 0 | 3109.3191 | 3109.3193 | −0.0002 |
| 11 | 0 | 1 | 12 | 0 | 0 | 3109.3223 | 3109.3210 | 0.0013 |
| 8 | 1 | 1 | 9 | 1 | 0 | 3109.6105 | 3109.6097 | 0.0008 |
| 8 | 0 | 1 | 9 | 0 | 0 | 3109.6112 | 3109.6115 | −0.0003 |
| 7 | 3 | 1 | 8 | 3 | 0 | 3109.6898 | 3109.6902 | −0.0004 |
| 7 | 2 | 1 | 8 | 2 | 0 | 3109.6985 | 3109.6988 | −0.0003 |
| 7 | 1 | 1 | 8 | 1 | 0 | 3109.7040 | 3109.7040 | 0.0000 |
| 7 | 0 | 1 | 8 | 0 | 0 | 3109.7055 | 3109.7057 | −0.0002 |
| 1 | 1 | 1 | 2 | 1 | 0 | 3110.2421 | 3110.2421 | 0.0000 |
| 1 | 0 | 1 | 2 | 0 | 0 | 3110.2449 | 3110.2439 | 0.0010 |
| 1 | 0 | 1 | 0 | 0 | 0 | 3110.5005 | 3110.4955 | 0.0050 |
| 2 | 1 | 1 | 1 | 1 | 0 | 3110.5771 | 3110.5750 | 0.0021 |
| 2 | 0 | 1 | 1 | 0 | 0 | 3110.5777 | 3110.5767 | 0.0010 |
| 3 | 2 | 1 | 2 | 2 | 0 | 3110.6504 | 3110.6497 | 0.0007 |
| 3 | 1 | 1 | 2 | 1 | 0 | 3110.6550 | 3110.6550 | 0.0000 |
| 3 | 0 | 1 | 2 | 0 | 0 | 3110.6575 | 3110.6567 | 0.0008 |
| 4 | 3 | 1 | 3 | 3 | 0 | 3110.7196 | 3110.7197 | −0.0001 |
| 4 | 2 | 1 | 3 | 2 | 0 | 3110.7280 | 3110.7284 | −0.0004 |
| 4 | 1 | 1 | 3 | 1 | 0 | 3110.7335 | 3110.7336 | −0.0001 |
| 4 | 0 | 1 | 3 | 0 | 0 | 3110.7355 | 3110.7354 | 0.0001 |
| 7 | 2 | 1 | 6 | 2 | 0 | 3110.9564 | 3110.9567 | −0.0003 |
| 7 | 1 | 1 | 6 | 1 | 0 | 3110.9620 | 3110.9619 | 0.0001 |
| 7 | 0 | 1 | 6 | 0 | 0 | 3110.9647 | 3110.9637 | 0.0010 |
| 8 | 1 | 1 | 7 | 1 | 0 | 3111.0349 | 3111.0354 | −0.0005 |
| 8 | 0 | 1 | 7 | 0 | 0 | 3111.0365 | 3111.0372 | −0.0007 |
| 12 | 1 | 1 | 11 | 1 | 0 | 3111.3152 | 3111.3165 | −0.0013 |
| 12 | 0 | 1 | 11 | 0 | 0 | 3111.3176 | 3111.3183 | −0.0007 |
| 14 | 4 | 1 | 13 | 4 | 0 | 3111.4223 | 3111.4228 | −0.0005 |
| 14 | 3 | 1 | 13 | 3 | 0 | 3111.4350 | 3111.4350 | 0.0000 |
| 14 | 2 | 1 | 13 | 2 | 0 | 3111.4440 | 3111.4439 | 0.0001 |
| 14 | 1 | 1 | 13 | 1 | 0 | 3111.4489 | 3111.4492 | −0.0003 |
| 14 | 0 | 1 | 13 | 0 | 0 | 3111.4505 | 3111.4510 | −0.0005 |
| 17 | 3 | 1 | 16 | 3 | 0 | 3111.6235 | 3111.6243 | −0.0008 |
| 17 | 2 | 1 | 16 | 2 | 0 | 3111.6322 | 3111.6332 | −0.0010 |
| 17 | 1 | 1 | 16 | 1 | 0 | 3111.6380 | 3111.6386 | −0.0006 |
| 17 | 0 | 1 | 16 | 0 | 0 | 3111.6389 | 3111.6404 | −0.0015 |
| 22 | 2 | 1 | 21 | 2 | 0 | 3111.9235 | 3111.9227 | 0.0008 |
| 22 | 1 | 1 | 21 | 1 | 0 | 3111.9272 | 3111.9282 | −0.0010 |
| 22 | 0 | 1 | 21 | 0 | 0 | 3111.9337 | 3111.9301 | 0.0036 |
| 23 | 3 | 1 | 22 | 3 | 0 | 3111.9678 | 3111.9676 | 0.0002 |
| 23 | 2 | 1 | 22 | 2 | 0 | 3111.9759 | 3111.9767 | −0.0008 |
| 23 | 1 | 1 | 22 | 1 | 0 | 3111.9810 | 3111.9823 | −0.0013 |
| 23 | 0 | 1 | 22 | 0 | 0 | 3111.9849 | 3111.9841 | 0.0008 |
| 25 | 3 | 1 | 24 | 3 | 0 | 3112.0724 | 3112.0717 | 0.0008 |
| 25 | 2 | 1 | 24 | 2 | 0 | 3112.0819 | 3112.0808 | 0.0011 |
| 25 | 1 | 1 | 24 | 1 | 0 | 3112.0853 | 3112.0864 | −0.0011 |
| 25 | 0 | 1 | 24 | 0 | 0 | 3112.0881 | 3112.0882 | −0.0001 |
| 26 | 2 | 1 | 25 | 2 | 0 | 3112.1318 | 3112.1309 | 0.0009 |
| 26 | 1 | 1 | 25 | 1 | 0 | 3112.1371 | 3112.1365 | 0.0006 |
| 26 | 0 | 1 | 25 | 0 | 0 | 3112.1378 | 3112.1384 | −0.0006 |
| 27 | 1 | 1 | 26 | 1 | 0 | 3112.1861 | 3112.1853 | 0.0008 |
| 27 | 0 | 1 | 26 | 0 | 0 | 3112.1876 | 3112.1872 | 0.0004 |
| 31 | 2 | 1 | 30 | 2 | 0 | 3112.3623 | 3112.3617 | 0.0006 |
| 31 | 1 | 1 | 30 | 1 | 0 | 3112.3678 | 3112.3674 | 0.0004 |
| 31 | 0 | 1 | 30 | 0 | 0 | 3112.3692 | 3112.3693 | −0.0001 |
| 32 | 3 | 1 | 31 | 3 | 0 | 3112.3951 | 3112.3945 | 0.0006 |
| 32 | 2 | 1 | 31 | 2 | 0 | 3112.4045 | 3112.4040 | 0.0005 |
| 32 | 1 | 1 | 31 | 1 | 0 | 3112.4101 | 3112.4097 | 0.0004 |
| 32 | 0 | 1 | 31 | 0 | 0 | 3112.4120 | 3112.4116 | 0.0004 |
| 35 | 3 | 1 | 34 | 3 | 0 | 3112.5119 | 3112.5132 | −0.0013 |
| 35 | 2 | 1 | 34 | 2 | 0 | 3112.5232 | 3112.5228 | 0.0004 |
| 35 | 1 | 1 | 34 | 1 | 0 | 3112.5289 | 3112.5286 | 0.0003 |
| 35 | 0 | 1 | 34 | 0 | 0 | 3112.5309 | 3112.5306 | 0.0004 |
| 38 | 4 | 1 | 37 | 4 | 0 | 3112.6060 | 3112.6066 | −0.0006 |
| 38 | 3 | 1 | 37 | 3 | 0 | 3112.6209 | 3112.6200 | 0.0009 |
| 38 | 2 | 1 | 37 | 2 | 0 | 3112.6279 | 3112.6298 | −0.0019 |
| 38 | 1 | 1 | 37 | 1 | 0 | 3112.6361 | 3112.6357 | 0.0004 |
| 38 | 0 | 1 | 37 | 0 | 0 | 3112.6380 | 3112.6377 | 0.0003 |
| 39 | 2 | 1 | 38 | 2 | 0 | 3112.6628 | 3112.6628 | 0.0000 |

**TABLE 2 (Continued)**

| $J'$ | $K'$ | $v'$ | $J''$ | $K''$ | $v''$ | measured | calculated | M−C | $J'$ | $K'$ | $v'$ | $J''$ | $K''$ | $v''$ | measured | calculated | M−C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | 1 | 1 | 17 | 1 | 0 | 3108.8089 | 3108.8093 | −0.0004 | 39 | 1 | 1 | 38 | 1 | 0 | 3112.6691 | 3112.6688 | 0.0004 |
| 16 | 0 | 1 | 17 | 0 | 0 | 3108.8110 | 3108.8110 | 0.0000 | 39 | 0 | 1 | 38 | 0 | 0 | 3112.6698 | 3112.6707 | −0.0009 |
| 12 | 5 | 1 | 13 | 5 | 0 | 3109.1769 | 3109.1792 | −0.0023 | 44 | 5 | 1 | 43 | 5 | 0 | 3112.7685 | 3112.7665 | 0.0020 |
| 12 | 4 | 1 | 13 | 4 | 0 | 3109.1944 | 3109.1942 | 0.0003 | 44 | 4 | 1 | 43 | 4 | 0 | 3112.7844 | 3112.7841 | 0.0003 |
| 12 | 3 | 1 | 13 | 3 | 0 | 3109.2055 | 3109.2060 | −0.0005 | 44 | 3 | 1 | 43 | 3 | 0 | 3112.7981 | 3112.7980 | 0.0001 |
| 12 | 2 | 1 | 13 | 2 | 0 | 3109.2152 | 3109.2147 | 0.0006 | 44 | 2 | 1 | 43 | 2 | 0 | 3112.8070 | 3112.8081 | −0.0011 |
| 12 | 1 | 1 | 13 | 1 | 0 | 3109.2198 | 3109.2199 | −0.0001 | 44 | 1 | 1 | 43 | 1 | 0 | 3112.8132 | 3112.8142 | −0.0010 |
| 12 | 0 | 1 | 13 | 0 | 0 | 3109.2215 | 3109.2216 | −0.0001 | 44 | 0 | 1 | 43 | 0 | 0 | 3112.8169 | 3112.8163 | 0.0006 |
| 11 | 2 | 1 | 12 | 2 | 0 | 3109.3152 | 3109.3141 | 0.0011 | | | | | | | | | |

[a] All of the frequency values are in $cm^{-1}$ units and $\sigma_{FIT}$ is 0.0022 $cm^{-1}$.

**TABLE 3: Structural Parameters Obtained for the CpNiNO Complex Using Least-Squares Fits**

| | experimental values | | theoretical values[a] | | |
|---|---|---|---|---|---|
| | this study | previous studies | Hay−Wadt | LANL2DZ | SDD |
| $\nu_0$ | 3110.4129(4) | 3110[b] | 3144 | 3194 | 3191 |
| $A''$ | [0.1459][c] | | 0.1459 | 0.1437 | 0.1436 |
| $B'' = C''$ | [0.04200487(2)][d] | 0.04200487(2)[d] | 0.04140 | 0.04002 | 0.04121 |
| $D_{J''}$ (kHz) | [0.08][d] | 0.08(2)[d] | | | |
| $D_{JK''}$ (kHz) | [2.70][d] | 2.70(6)[d] | | | |
| $D_{K''}$ (kHz) | [0.00] | | | | |
| $A'$ | 0.14328(8) | | 0.1458 | 0.1436 | 0.1435 |
| $B' = C'$ | 0.041285(1) | | 0.04138 | 0.04000 | 0.04119 |
| $D_{J'}$ (kHz) | 0.078(1) | | | | |
| $D_{JK'}$ (kHz) | 2.23(4) | | | | |
| $D_{K'}$ (kHz) | −2.63(2) | | | | |
| $N$ | 155 | | | | |
| $\sigma$ ($cm^{-1}$) | 0.0022 | | | | |

[a] The theoretical values obtained using the rB3PW91 level; three different basis sets are presented for comparison. The listed values are in $cm^{-1}$ (unless otherwise mentioned), and error limits are 1$\sigma$. Values in brackets were held fixed to previous FTMW and best DFT values. [b] Frequency obtained from a low-resolution infrared experiment.[13] [c] Fixed to DFT value. [d] The values were held fixed to the gas-phase FTMW values[11] during the fit.

**TABLE 4: Calculated Lower State Combination Differences (LSCD = Combination Differences with a Common Upper State) for Various Rotational States[a]**

| | frequency ($cm^{-1}$) | | | |
|---|---|---|---|---|
| upper $J$ state | $R$-branch | $P$-branch | $B''$ | $K$ state |
| 39 | 3112.6698 | 3106.0569 | 0.041854 | 0 |
| | 3112.6691 | 3106.0425 | 0.041941 | 1 |
| | 3112.6628 | 3106.0371 | 0.041935 | 2 |
| 38 | 3112.6380 | 3106.1776 | 0.041951 | 0 |
| | 3112.6361 | 3106.1778 | 0.041937 | 1 |
| | 3112.6279 | 3106.1719 | 0.041922 | 2 |
| | 3112.6209 | 3106.1635 | 0.041931 | 3 |
| | 3112.6060 | 3106.1468 | 0.041943 | 4 |
| 26 | 3112.1373 | 3107.6924 | 0.041933 | 0 |
| | 3112.1371 | 3107.6908 | 0.041946 | 1 |
| | 3112.1318 | 3107.6858 | 0.041943 | 2 |
| 22 | 3111.9337 | 3108.1555 | 0.041980 | 0 |
| | 3111.9272 | 3108.1538 | 0.041927 | 1 |
| 12 | 3111.3176 | 3109.2215 | 0.041922 | 0 |
| | 3111.3152 | 3109.2198 | 0.041908 | 1 |
| 8 | 3111.0365 | 3109.6112 | 0.041921 | 0 |
| | 3111.0349 | 3109.6105 | 0.041894 | 1 |
| 7 | 3110.9647 | 3109.7055 | 0.041973 | 0 |
| | 3110.9620 | 3109.7040 | 0.041933 | 1 |
| | 3110.9564 | 3109.6985 | 0.041930 | 2 |

[a] The $B''$ values were calculated using LSCD formula $\Delta F(J) = 4B''(J + 1/2)$. As shown, the consistency of the value for the lower ground state rotational, $B''$ constant, provides further support to the fit.

the ground state rotational constant $B''$ (FTMW value),[11] and this trend has been observed in the current DFT calculated values and would be an expected effect of vibrational averaging for an excited vibrational state. The calculated constants differ from the current experimental results by 1−3%, but we believe that these calculated values can be improved to near experimental values if one were to include vibration averaging corrections and use a larger basis set for the Ni atom. A larger basis set for the Ni atom would hopefully provide more accurate rotational constants and vibrational frequencies. The C−H stretching frequencies for the Cp moiety depend on the strength of the $\pi$-bonding between the Cp and the Ni atom. The differences between ground- and excited-state rotational constants were as expected, and this is caused by an increase in average internuclear distance in the upper vibrational state. The best fit, with a standard deviation of 0.0022 $cm^{-1}$, was obtained by constraining the ground-state distortion constants ($D_{J''}$, $D_{JK''}$, and $D_{K''}$) to the previous FTMW results, while treating the distortion constants for the vibrational excited state ($D_{J'}$, $D_{JK'}$, and $D_{K'}$) as adjustable parameters. We believe that this is a reasonable approach because distortion constant values may be affected by other low-lying vibrational levels. Attempts to fit the measured lines by keeping the same distortion constants for both ground and excited vibrational states resulted in a much higher standard deviation for the fit. The upper state distortion constant, $D_{J'}$, obtained from the current analysis, is very close to the previously reported microwave value of 0.08(2) kHz. However, $D_{JK'}$ for the upper state shows a significant decrease when compared to the microwave value (see Table 3). This is probably due to more readily distorted bond angles in the upper state as compared to the lower state. An inclusion of an additional distortion constant ($D_{K'}$) further improved the fit deviation. In this case, the ground-state $D_{K''}$ value held fixed to zero because neither DFT nor FTMW values are available for this constant.

The line broadening in the spectra is probably a combination of both Doppler and pressure broadening.

$$\Delta\nu(\text{fwhm}) = 7.1 \times 10^{-7} \times \nu_0 \times \sqrt{(T/M)} \qquad (2)$$

The Doppler broadening can be calculated from eq 2, where $\Delta\nu$ is the width of the line in cm$^{-1}$ at half the peak height (fwhm), $\nu_0$ is the line center in cm$^{-1}$, $T$ is the temperature of the cell (room temperature in our case) in Kelvin, and $M$ is the molecular weight in atomic mass units. According to this analysis, the predicted Doppler broadening of the lines that we measured is approximately 0.0043 cm$^{-1}$. Pressure broadening is more difficult to estimate, but according to gas kinetic theory, this is approximately 0.00033 cm$^{-1}$ per Torr for hard sphere collisions. However, this underestimates the value, by an order of magnitude or more, for large polyatomic molecules. Because the approximate vapor pressure of the sample used in the experiment was 100−150 Torr, the pressure broadening due to sample pressure will be a significant factor for the line width observed. Therefore, we believe that the spectra observed at resolution 0.006 cm$^{-1}$ are already at the Doppler and/or pressure-broadened resolution limit. Furthermore, judging the appearance of the lines in the spectra, we believe that it is highly unlikely that recording the spectra of these large polyatomic molecules with higher instrumental resolution, on the order of 0.001 cm$^{-1}$, would resolve any further structure in the spectra, when using a static gas cell.

## Conclusions

The gas-phase rotational constants and distortion constants for the excited vibrational state ($v = 1$) corresponding to the $\nu_1$ vibrational band involving the symmetric C−H stretching vibration have been determined using high-resolution Fourier transform infrared spectroscopy. The analysis also yields the C−H symmetric vibrational stretching frequency ($\nu_1$) for the CpNiNO transition metal complex. The observed values are much more accurate and precise but agree well with the previously measured experimental values and current theoretical values. The rotational constants obtained from the current study are only about 2% different between the ground and the excited state and suggest that the structure of this molecule is not changed significantly in the excited vibrational state. Very small distortion constants obtained for both the ground and the excited states suggest that CpNiNO is a rigid molecule in both states.

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