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Ni₂ revisited: Reassignment of the ground electronic state

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Resonant two-photon ionization spectroscopy was used to study jet-cooled Ni₂ produced by pulsed laser ablation of a nickel target in the throat of a supersonic nozzle using argon as the carrier gas. Spectral regions previously investigated using helium as the carrier gas were reinvestigated, and the improved cooling achieved was found to suppress transitions arising from an $\Omega=4$ state that had been thought to be the ground state. Seven new vibronic progressions were assigned, with spectroscopic constants determined for the excited states. The predissociation threshold in Ni₂ was reinvestigated, and a revised value for the binding energy is given as $D_0^\circ(\text{Ni}_2)=2.042\pm0.002$ eV. The ionization energy of Ni₂ was found to be 7.430 ± 0.025 eV, and from this result and the revised bond dissociation energy of the neutral, the binding energy of the cation was calculated to be $D_0^\circ(\text{Ni}_2^+)=2.245\pm0.025$ eV. Similarly, $D_0^\circ(\text{Ni}_2^-)=1.812\pm0.014$ eV is obtained using $D_0^\circ(\text{Ni}_2)$ and the electron affinities of Ni and Ni₂. Twenty bands were rotationally resolved, all originating from a lower state of $\Omega''=0_g^+$ or 0_u^- which we argue is the true ground state, in agreement with ligand field and *ab initio* theoretical studies. The rotational analysis also yielded a ground state bond length of 2.1545 ± 0.0004 Å for $^{58}\text{Ni}_2$. © 1995 American Institute of Physics.

I. INTRODUCTION

Owing to the importance of nickel as a catalyst, nickel containing molecules have been widely studied by both theoreticians and experimentalists. Nickel and transition metals in general, are challenging to study in that the open *3d* subshells can lead to complicated electronic structures. A detailed understanding of Ni₂, as the simplest nickel cluster, is an important first step in understanding how the bonding in nickel evolves as one moves from the atom to the bulk metal. It is therefore not surprising that Ni₂ has been extensively studied by both theoretical^{1–11} and experimental^{12–18} techniques.

Due to the contracted nature of the *3d* orbitals in Ni, and the more diffuse nature of the *4s* orbitals, the *3d* orbitals are not expected to contribute significantly to the bonding in Ni₂. The separated atom limit lying lowest in energy arises from two $3d^8 4s^2(^3F_4)$ Ni atoms. Because the filled *4s* orbitals are ill suited for bonding, chemical bonding requires promotion of one or both atoms to the $3d^9 4s^1(^3D_3)$ configuration, which lies only 204.786 cm^{–1} above the ground 3F_4 level. A ground manifold of 59 distinct electronic states (41 of which are doubly degenerate), all described as $3d_A^9 3d_B^9 \sigma_g^2$ but differing in the location and spin coupling of the *3d* hole on each atom, arises from the $3d_A^9 4s_A^1(^3D)+3d_B^9 4s_B^1(^3D)$ separated atom limit. Furthermore, due to the close proximity of these states in energy, spin–orbit interactions are expected to mix them thoroughly, leaving only Ω , *g/u*, and $0^+/0^-$ as good quantum numbers in Hund's case (c).

This manifold of states has been calculated both by ligand field¹ and *ab initio* methods.^{2–11} To our knowledge, only the ligand field calculation and one *ab initio*³ study have included a full treatment of spin–orbit interactions for all 59 distinct states. The theoretical studies predict the *3d* hole in each nickel $3d^9$ core to be located in the *dδ* orbital in the ground electronic state, consistent with the idea that the *3d* orbitals are not split into bonding and antibonding orbitals. If

d orbital contributions to the bonding were significant, an orbital ordering of the *3d*-based molecular orbitals of $\sigma_g < \pi_u < \delta_g < \delta_u^* < \pi_g^* < \sigma_u^*$ would be expected, favoring placement of the holes in σ_u^* or π_g^* orbitals. In the absence of spin–orbit interactions the placement of both holes in *dδ* orbitals produces $^3\Sigma_u^+$, $^3\Sigma_g^+$, $^1\Sigma_u^+$, $^1\Sigma_g^+$, $^3\Gamma_u$, and $^1\Gamma_g$ molecular states, which are calculated to be nearly degenerate. The ground state predicted by *ab initio*³ methods including spin–orbit interactions is $\Omega=0_g^+$ (a mix of the $^3\Sigma_g^+$ and the $^1\Sigma_g^+$ states), with an $\Omega=0_u^-$ state (a mix of the $^3\Sigma_u^+$ and $^1\Sigma_u^+$ states) and an $\Omega=5_u$ ($^3\Gamma_u$) state only 12 and 58 cm^{–1} higher in energy, respectively. Ligand field theory¹ has predicted the same 0_g^+ , 0_u^- , and 5_u states as the lowest states, but these are now calculated to be precisely degenerate within the framework of the theory. Indeed, when the ligand field and *ab initio* results are compared for all the calculated states, they agree remarkably well. This agreement between two very different theoretical methods would tend to indicate that the simple, intuitive model of the ligand field theory describes Ni₂ well. Previous experimental work, however, disagrees with these theoretical predictions.

Several experimental studies of Ni₂ have been performed in argon matrices. DeVore, *et al.*¹² reported a single absorption system with an average vibrational spacing of 192 cm^{–1}, and the 0-0 band at 21 786 cm^{–1}. Moskovits and Hulse,¹³ however, found two discrete band systems with origins at 18 920 and 26 500 cm^{–1}, and a continuous band peaking at 24 000 cm^{–1}, although they did not see the band at 21 786 cm^{–1} that DeVore had reported. Ahmed and Nixon¹⁴ dispersed the fluorescence from what they thought was the C–X system (as assigned by Moskovits and Hulse), and obtained an isotopically resolved spectrum with $\omega_e'' = 380.9$ cm^{–1}, $\omega_e x_e'' = 1.08$ cm^{–1}, and $\nu_{00}=22\,246$ cm^{–1} for $^{58}\text{Ni}_2$. Rasanen, Heimbrook, and Bondybey¹⁵ later showed that this spectrum was in fact caused by an impurity in Ahmed and Nixon's samples by successfully fitting the spectrum to Se₂.

A recent study by Ho *et al.*¹⁶ employing photoelectron spectroscopy of Ni₂⁺ produced using a mixture of argon and helium as the carrier gas in a flowing afterglow ion source determined information for the neutral as well. For Ni₂, the value of $\omega_e'' = 280 \pm 20 \text{ cm}^{-1}$ was determined for the ground state.

The binding energy of Ni₂, $D_0^{\circ}(\text{Ni}_2)$, was first estimated to be $2.03 \pm 0.30 \text{ eV}$ and $2.36 \pm 0.22 \text{ eV}$ by Kant¹⁷ using second and third law analyses, respectively, of Knudsen effusion mass spectrometric data. A more precise determination of the binding energy was made by Morse *et al.*,¹⁸ who reported the first gas-phase electronic spectrum of nickel dimer. Resonant two-photon ionization spectroscopy employing time-of-flight mass spectrometric detection was used to study Ni₂ cooled in a supersonic beam using helium as the carrier gas, and the binding energy of Ni₂ was determined to be $2.068 \pm 0.010 \text{ eV}$ through the observation of an abrupt predissociation threshold. In the same study, the first rotationally resolved spectrum of Ni₂ was reported. A single band at 8751 \AA ($\approx 11\,430 \text{ cm}^{-1}$) was analyzed and assigned unambiguously as an $\Omega' = 5 \leftarrow \Omega'' = 4$ transition, yielding a ground state bond length of $2.200 \pm 0.007 \text{ \AA}$, and a ground state electronic symmetry of either $^1\Gamma_g$ or $^3\Gamma_u$ in Hund's case (a). Furthermore, in an unpublished study, a high resolution scan over a band at $11\,523 \text{ cm}^{-1}$ was performed in this laboratory by Spain, who observed the transition in Ni₂ during a study of the 0-0 band of the $A[11.5]2.5 \leftarrow X^2\Delta_{5/2}$ system of NiCu.¹⁹ This band was also studied using helium as the carrier gas, and assigned as an $\Omega' = 5 \leftarrow \Omega'' = 4$ transition. These results agree with the theoretical calculations in the absence of spin-orbit interactions in that they place the $3d$ holes in a $\delta\delta$ configuration for the ground state. However, the inclusion of spin-orbit interactions in either the ligand field or the *ab initio* calculations leads to the prediction that the lowest state with $\Omega = 4$ lies roughly 800 cm^{-1} above the ground state in Ni₂.

Theory predicts a high density of states (59 distinct potential energy surfaces lying within 1 eV of the ground state) in Ni₂, and the possibility exists that unquenched low lying excited states might be observed under conditions that would normally be expected to cool molecules to their ground electronic states. If this were the case, previously reported ground state information could be incorrect. The major purpose of the present investigation was to determine if this was the case for Ni₂, and if so to determine conclusively the ground state symmetry for this molecule.

II. EXPERIMENT

Resonant two-photon ionization spectroscopy with time-of-flight mass spectrometric detection was used to investigate supersonically cooled nickel dimer molecules. Experimental details have been described previously.²⁰ The Ni₂ molecules were formed by pulsed laser vaporization (Nd:YAG, 532 nm, 15–20 mJ/mm²) of a Ni disk, followed by supersonic expansion in argon carrier gas (150 psia). The beam of jet-cooled molecules was collimated by a skimmer before entering the spectroscopic interrogation and ionization region of a reflectron time-of-flight mass spectrometer.

The frequency range from $10\,000$ to $12\,100 \text{ cm}^{-1}$ was

investigated in low resolution ($\approx 0.7 \text{ cm}^{-1}$) by Raman shifting the output of the excitation laser, a Nd:YAG pumped tunable dye laser operating with R640:DCM 1:1 mix, DCM:LDS 698 1:1 mix, and LDS 698 laser dyes, using a stainless-steel cell pressurized with approximately 500 psi of H₂ gas. A low-pass filter blocked the fundamental and anti-Stokes light, leaving only the first Stokes Raman shifted light (shifted by $-4155.163 \text{ cm}^{-1}$) (Ref. 21) to excite the molecule. The frequency ranges from $12\,100$ to $14\,400 \text{ cm}^{-1}$ and $16\,300$ to $16\,800 \text{ cm}^{-1}$ were interrogated using the unshifted output of the excitation laser operating with LDS 821, LDS 751:821 1.5:1 mix, LDS 751, LDS 750, LDS 698, R640, R640:DCM 1:1 mix, and R610:R640 3:1 mix laser dyes. A fixed frequency excimer laser (ArF, 193 nm, 6.42 eV) was used for photoionization of the excited molecules for all energy regions. In the determination of the ionization energy the region from $12\,100$ to $14\,400 \text{ cm}^{-1}$ was reinvestigated using the Raman shifted output of the excimer laser (first Stokes from H₂, 210 nm, 5.90 eV) as the ionization photon.

Twenty-three bands were examined under high resolution ($\approx 0.04 \text{ cm}^{-1}$) while an absorption spectrum of gaseous I₂ was recorded simultaneously for calibration. This was accomplished by narrowing the output of the dye laser by insertion of an air-spaced intracavity étalon, which was then pressure scanned with CCl₂F₂ (Freon 12, DuPont). The I₂ atlas of Gerstenkorn and Luc²² was used to provide absolute frequency calibration.

In order to determine the effect of the carrier gas on the observed spectrum of Ni₂, the energy region of $10\,000$ to $12\,100 \text{ cm}^{-1}$ was investigated in low resolution using helium as the carrier gas in the supersonic expansion. To maximize the signal, the timing of the vaporization of metal in the pulse of carrier gas was changed by $100 \mu\text{s}$, so that for helium the sample was vaporized earlier in time, closer to the beginning of the helium pulse. All other experimental conditions were nearly identical to the experiments using argon carrier gas, except that a lower vaporization power was used and an extender was attached to the nozzle channel to enhance cooling in the helium experiments. The extender added 5 mm in length to the nozzle channel and decreased the diameter of the final expansion orifice to 2 mm.

As described in Sec. I, the high resolution study of the band at $11\,523 \text{ cm}^{-1}$ was performed previously. Helium was used as the carrier gas in that study, and a detailed description of the experimental conditions has been previously given.¹⁹

III. RESULTS

A. Low resolution spectrum of Ni₂

1. Identification of band systems

Figure 1 presents a portion of the vibronic spectrum of $^{58}\text{Ni}_2$, taken using argon as the carrier gas in the supersonic expansion. Seven band systems have been found in the energy region of $10\,000$ to $12\,550 \text{ cm}^{-1}$. The band positions, vibrational assignments, spectroscopic constants, and isotope shift information are listed in Table I. To label the electronic states, we have adopted the nomenclature in which the excited electronic states are identified by the energy of the

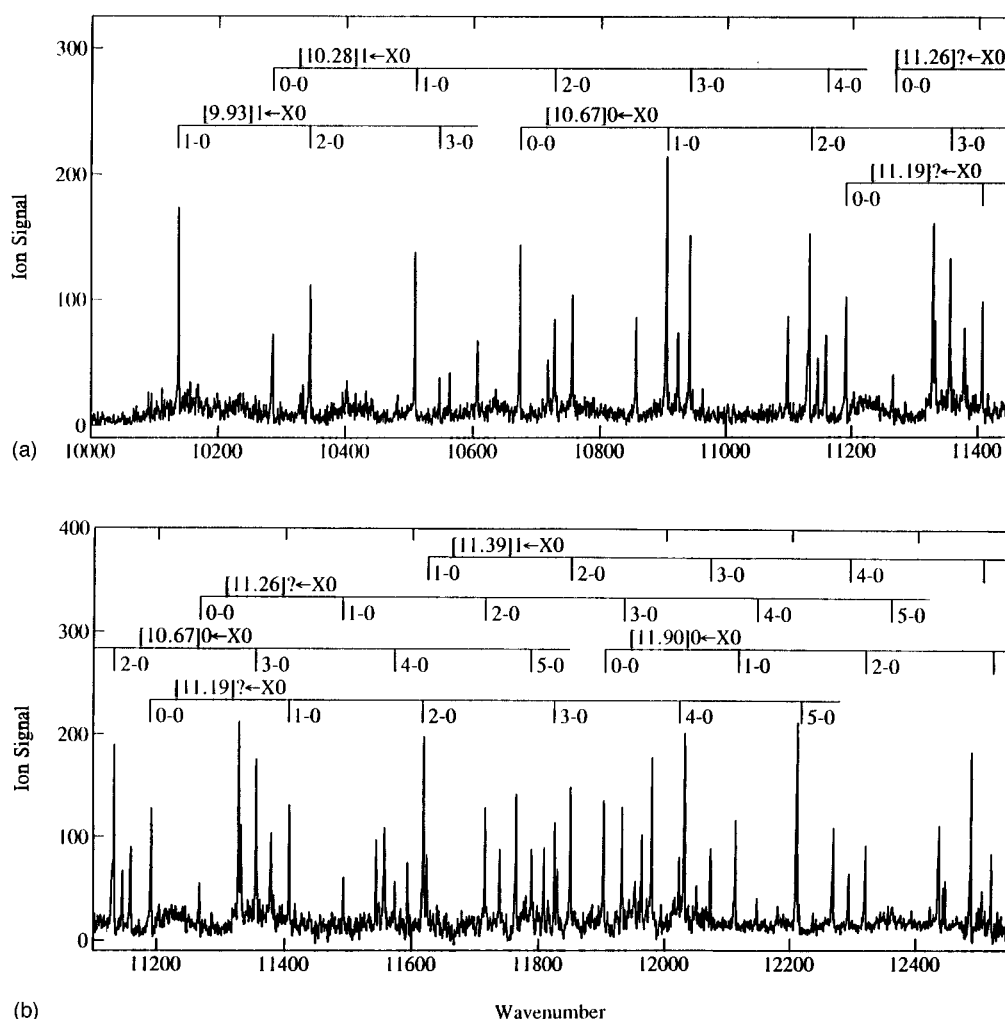


FIG. 1. Low resolution spectra of $^{58}\text{Ni}_2$ recorded using Ar carrier gas and ArF excimer radiation for photoionization from (a) 10 000 to 11 450 cm^{-1} and (b) 11 100 to 12 550 cm^{-1} .

$v'=0$ level above the $v''=0$ level of the ground state in square brackets (in thousands of wave numbers, cm^{-1}), followed by the Ω value of the state. In cases where the Ω value is undetermined because none of the bands of the system were rotationally resolved, a question mark is used. This nomenclature, originally introduced for the spectra of the rare earth oxides,²³ is particularly appropriate for these transitions. Three bands in the UV have already been labeled using the letters A, B, and C, so the common spectroscopic practice of using letters to label the states would be at best impractical. Based on the evidence that effective cooling of the molecular beam has been achieved (presented in Sec. III A 2), the lower state of systems that were not rotationally resolved has been assumed to be the ground $\Omega=0$ state.

A manifold of states which may be described as $3d_A^9(^2D)3d_B^8(^3F)\sigma_g^2\sigma_u^*$ states arises from the $3d_A^94s_A^1(^3D)+3d_B^84s_B^2(^3F)$ separated atom limit, which is nearly degenerate with the $^3D+^3D$ and $^3F+^3F$ separated atom limits. We believe that the upper states of the observed transitions belong to this $3d_A^9(^2D)3d_B^8(^3F)\sigma_g^2\sigma_u^*$ manifold of states. Because little or no d orbital contributions to the bonding are expected, states in this manifold will have an approximate

bond order of 0.5, and are therefore expected to have longer bond lengths and smaller vibrational frequencies than the ground manifold of states. This is consistent with our experimental observations. The excited state vibrational frequencies obtained by fitting observed progressions ranged from 209 to 233 cm^{-1} , which may be compared to the ground state vibrational frequency of $280\pm 20 \text{ cm}^{-1}$ obtained by Ho *et al.*¹⁶ Rotational analysis determined that the bond did indeed lengthen upon excitation, as is shown in Section III B of this article.

2. Evidence of cooling

It has been suggested that the discrepancy between the previous experimental determination¹⁸ of the ground state of the nickel dimer as $\Omega=4$ and the theoretically predicted^{1,3} ground state of $\Omega=0_g^+$, 0_u^- , or 5_u might be explained by inefficient cooling of the Ni_2 molecules, leading to the incorrect assignment of a low lying excited electronic state as the ground state. Both the ligand field and *ab initio* results predict $\Omega=4_g$ and 4_u states approximately 830 cm^{-1} above the ground state. It seems likely that it would be difficult to

TABLE I. Assigned vibronic band systems of ⁵⁸Ni₂.

System	Band	Frequency ^a (cm ⁻¹)	Isotope shift ^b (cm ⁻¹)		Spectroscopic constants ^c		
			⁵⁸ Ni; ⁶⁰ Ni	⁶⁰ Ni; ⁶⁰ Ni	⁵⁸ Ni; ⁵⁸ Ni	⁵⁸ Ni; ⁶⁰ Ni	⁶⁰ Ni; ⁶⁰ Ni
[9.93]1←X0	1-0	10134.5747 ^{d,e}	1.2468 ^{d,e}	2.5109 ^{d,e}	$T_0=9927.39^e$	$T_0=9928.24^e$	$T_0=9928.09^e$
	2-0	10339.45 ^e	2.78 ^e	5.33 ^e	$\omega'_e=209.50^e$	$\omega'_e=206.83^e$	$\omega'_e=205.89^e$
	3-0	10542.01 ^e	3.75 ^e	7.74 ^e	$\omega'_ex'_e=1.16^e$	$\omega'_ex'_e=0.87^e$	$\omega'_ex'_e=0.96^e$
[10.28]1←X0	0-0 ^g	10282.38(−43)	0.60(−09)	0.61(−30)	$T_0=10\,282.81(121)$	$T_0=10\,281.87(33)$	$T_0=10\,282.07(66)$
	1-0 ^g	10506.42(66)	2.17(29)	4.17(58)	$\omega'_e=226.42(176)$	$\omega'_e=225.72(49)$	$\omega'_e=222.61(96)$
	2-0 ^g	10725.79(56)	3.70(−35)	7.48(06)	$\omega'_ex'_e=1.73(34)$	$\omega'_ex'_e=1.81(09)$	$\omega'_ex'_e=1.51(19)$
	3-0 ^g	10939.8332(−14090) ^d	2.3390(1840) ^{d,f}	8.68(−66)			
	4-0 ^g	11154.39(61)	5.87(−03)	11.70(32)			
[10.67]0←X0	0-0	10669.8785(−3880) ^d	−0.0150(−3170) ^d	−0.0760(−1330) ^d	$T_0=10\,670.27(48)$	$T_0=10\,670.21(45)$	$T_0=10\,670.09(58)$
	1-0	10901.3482(7200) ^d	1.8527 (6370) ^d	3.71(40)	$\omega'_e=234.03(54)$	$\omega'_e=232.34(51)$	$\omega'_e=231.13(122)$
	2-0	11127.2512(−0670) ^d	3.6727(−2340) ^d	7.22(−40)	$\omega'_ex'_e=1.84(09)$	$\omega'_ex'_e=1.85(08)$	$\omega'_ex'_e=1.99(30)$
	3-0	11350.10(−24)	4.97(05)	10.33(13)			
	4-0	11569.41(−27)	7.14(−37)				
	5-0	11785.59(24)	8.84(23)				
[11.19]?←X0	0-0	11185.71(20)	−0.13(33)	0.20(−25)	$T_0=11\,185.51(66)$	$T_0=11\,185.51(100)$	$T_0=11\,185.75(107)$
	1-0	11403.12(−21)	1.53(−25)	2.86(74)	$\omega'_e=224.12(74)$	$\omega'_e=222.99(113)$	$\omega'_e=219.39(225)$
	2-0	11614.26(−59)	3.70(−95)	7.32(−74)	$\omega'_ex'_e=3.15(12)$	$\omega'_ex'_e=3.33(18)$	$\omega'_ex'_e=2.81(55)$
	3-0	11821.07(100)	5.41(112)	10.61(25)			
	4-0	12018.59(−41)					
[11.26]?←X0	5-0	12211.65(01)	11.28(−24)				
	0-0	11262.83(10)	0.02(27)	0.06(09)	$T_0=11\,262.73(31)$	$T_0=11\,262.53(139)$	$T_0=11\,262.68(93)$
	1-0	11487.52(−07)			$\omega'_e=227.65(34)$	$\omega'_e=226.90(143)$	$\omega'_e=223.96(131)$
	2-0	11709.31(−34)	4.06(−82)	7.52(−53)	$\omega'_ex'_e=1.40(06)$	$\omega'_ex'_e=1.71(23)$	$\omega'_ex'_e=1.38(26)$
	3-0	11929.38(45)	6.89(−24)	10.66(71)			
	4-0	12145.31(−10)	7.75(159)	14.64(−27)			
[11.39]1←X0	5-0	12359.06(−04)	14.07(−80)				
	1-0 ^g	11620.04(17)	0.88(17)		$T_0=11\,390.42(84)$	$T_0=11\,392.15(76)$	$T_0=11\,390.22^e$
	2-0 ^g	11845.35(−40)	2.94(−37)	5.75 ^e	$\omega'_e=232.97(74)$	$\omega'_e=229.92(68)$	$\omega'_e=229.86^e$
	3-0 ^g	12068.28(16)	4.71(08)	9.16 ^e	$\omega'_ex'_e=1.76(10)$	$\omega'_ex'_e=1.54(10)$	$\omega'_ex'_e=1.72^e$
	4-0 ^g	12287.1549(1870) ^d	5.78(26)	12.06 ^e			
[11.90]0←X0	5-0 ^g	12502.19(−12)	6.65(−14)				
	0-0	11899.48(−17)	0.38(−21)	0.27 ^e	$T_0=11\,899.66(75)$	$T_0=11\,899.31(91)$	$T_0=11\,899.21^e$
	1-0	12109.70(52)	2.11(62)	4.30 ^e	$\omega'_e=213.12(158)$	$\omega'_e=211.54(191)$	$\omega'_e=211.51^e$
	2-0	12314.5776(−5190) ^d	4.4646(−6240) ^d	8.34 ^e	$\omega'_ex'_e=1.80(39)$	$\omega'_ex'_e=1.91(46)$	$\omega'_ex'_e=2.67^e$
	3-0	12517.59(17)	6.76(21)				

^aVibronic bands were fit to the formula $\nu = T_0 + \omega'_e v' - \omega'_ex'_e(v'^2 + v')$. The residual ($\nu_{\text{obs}} - \nu_{\text{calc}}$) is reported in parentheses after each entry in units of 0.01 cm⁻¹ for bands not rotationally resolved, and 0.0001 cm⁻¹ for bands that were rotationally resolved.

^bIsotope shifts are reported as $\nu(^{58}\text{Ni}_2) - \nu(\text{modification})$, and the residual ($\nu_{\text{obs}} - \nu_{\text{calc}}$) of the fits for the isotopic modifications is given in parentheses after each entry, in units of 0.01 cm⁻¹ for bands not rotationally resolved, and 0.0001 cm⁻¹ for bands rotationally resolved.

^cSpectroscopic constants are reported for each band system, with the 1 σ error limits given in parentheses in units of 0.01 cm⁻¹.

^dRotationally resolved bands, with absolute calibration based on the I₂ atlas of Gerstenkorn and Luc corrected for the Doppler shift experienced by the Ni₂ molecules as they traveled toward the light source.

^eSince only three bands were fit, it was not possible to estimate the error of the fit.

^fA second band 3.6 cm⁻¹ to the red of the 3-0 band was observed in the ⁵⁸Ni⁶⁰Ni isotopic combination that was not observed in the ⁵⁸Ni₂ or ⁶⁰Ni₂ spectra. It is likely that the two bands were perturbing each other, causing the isotope shift to be less than expected for this band.

^gVibrational numbering may be in error by one unit.

collisionally cool a molecule in a $\Omega=4$ electronic state to an $\Omega=0$ state, because this would require a complete reversal of the orbital angular momentum of a δ hole in the d^9 core of one of the nickel atoms. Because the compact d^9 cores are well shielded from the outside world by the relatively diffuse σ_g^2 pair of electrons, such a major change in λ seems unlikely. Similarly, the shielding of the d^9 cores from the external world by the σ_g^2 electrons may make a “ g ” to “ u ” conversion improbable, so that cooling an $\Omega=4_g$ state to an $\Omega=5_u$ state is likewise difficult. Because only two bands were rotationally resolved in the initial investigations, the possibility that these transitions could originate from an unquenched excited state seems plausible.

Argon has been used successfully in this laboratory to

enhance cooling of vibrational and electronic degrees of freedom,^{24,25} so an attempt to improve the cooling of Ni₂ was made using argon as the carrier gas in the expansion. Low resolution scans were recorded using helium as the carrier gas, and compared to the spectra obtained when argon was used. Figure 2 shows the region of the spectrum containing the band resolved by Morse *et al.*¹⁸ ($\Omega''=4$) and the band resolved previously in this laboratory ($\Omega''=4$). Both bands are present in the spectrum recorded using helium carrier gas (lower panel, Fig. 2), but vanish when argon carrier gas is employed (upper panel, Fig. 2). In addition, it is clear that all the bands observed in the argon scan are also present in the helium scan, even if observed only weakly. This was true of the entire region in which spectra were obtained using both

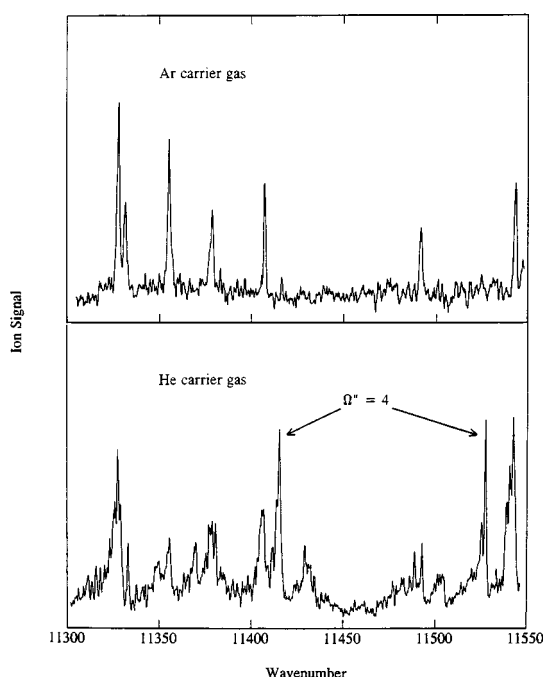


FIG. 2. Spectrum of $^{58}\text{Ni}_2$ recorded using argon carrier gas (upper panel) and helium carrier gas (lower panel). Two transitions originating from $\Omega''=4$ are identified in the lower panel. These are suppressed when argon carrier gas is used.

helium and argon ($10\,000$ to $12\,500\text{ cm}^{-1}$). In general, the spectra recorded using argon carrier gas were much less congested, and rotationally much cooler than those taken with helium. In addition, twenty bands in the spectrum recorded with argon used as the carrier gas were rotationally resolved and analyzed, as will be discussed in detail in Sec. III B. All twenty originated from the same lower state with $\Omega''=0_g^+$ or 0_u^- , suggesting strongly that they all originate from the ground state.

3. Predissociation threshold in Ni_2

In the previous study by Morse *et al.*,¹⁸ the excited state lifetimes of more than 20 transitions in the range of $16\,300$ – $17\,120\text{ cm}^{-1}$ were measured, with all the transitions to the red of $16\,680\text{ cm}^{-1}$ having lifetimes on the microsecond time scale. At $16\,680 \pm 10\text{ cm}^{-1}$ an abrupt change in the measured lifetimes was observed which was attributed to a predissociation threshold. Figure 3 displays the spectrum of $^{58}\text{Ni}_2$ taken first with a 20 ns delay between the excitation photon and the ionization photon (upper panel), and then with a 200 ns delay (lower panel). The excited state lifetimes of the last of the long-lived bands (at $16\,658.0\text{ cm}^{-1}$) was measured as $16 \pm 5\text{ }\mu\text{s}$; that of the first of the short-lived bands (at $16\,689.6\text{ cm}^{-1}$) was measured as $27 \pm 5\text{ ns}$. Because the positions of these two bands were calibrated using the iodine atlas of Gerstenkorn and Luc,²² this allowed the predissociation threshold to be accurately bracketed. At a minimum, the observation of a sharp predissociation threshold provides an upper limit to the binding energy of the molecule.

It has been argued, however,²⁶ that if the threshold is sharp and well defined, without evidence of Frank–Condon

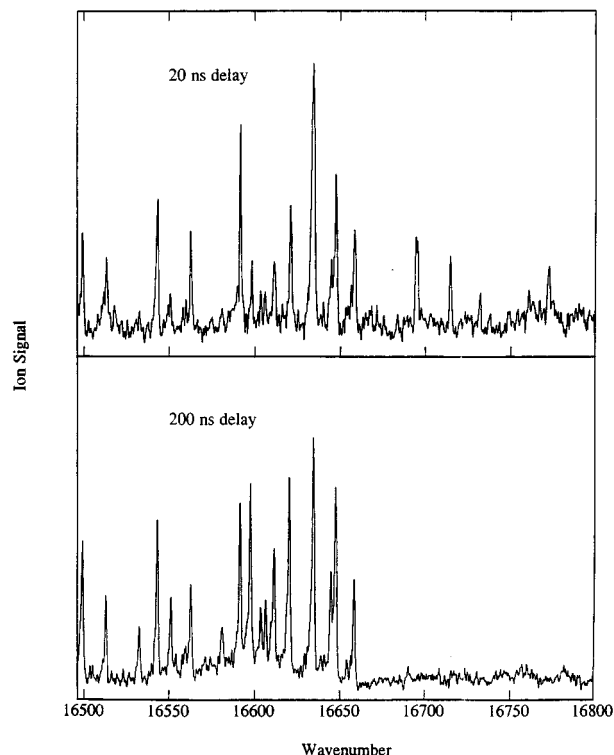


FIG. 3. Predissociation threshold in $^{58}\text{Ni}_2$. Experimental conditions were the same for the two scans with the exception that a 20 ns delay between the excitation and ionization lasers was used in the upper panel, and a 200 ns delay was used in the lower panel.

difficulties in either the excitation or predissociation step, if dissociation can occur to the ground separated atom limit while preserving the good quantum numbers, and if the ground separated atom limit generates a considerable number of molecular potential energy surfaces, some of which may be predicted to be repulsive, then the predissociation threshold provides an accurate value for the bond dissociation energy, D_0° . The basis for these criteria is that in molecules where the density of states is very large, mixing of states causes the breakdown of the Born–Oppenheimer approximation, excitation can no longer be thought of as occurring to a single potential energy surface, and mixing of bound states with dissociative states leads to the occurrence of predissociation as soon as the bond strength of the molecule is exceeded.

The first criterion, that the threshold is sharp and well defined, is met for Ni_2 , as can be observed in Fig. 3. In Ni_2 , the density of states is such that the states are well mixed by spin–orbit interactions, leaving only Ω , g/u , and in the case of $\Omega=0$, $+/-$ as good quantum numbers. From the states predicted to be lowest in energy, the $\Omega=0_g^+$, $\Omega=0_u^-$, and the $\Omega=5_u$ state, transitions to $\Omega=0_u^+$, 1_u , $\Omega=0_g^-$, 1_g , or $\Omega=4_g$, 5_g , 6_g are allowed. The ground separated atom limit ($^3\text{F}_4 + ^3\text{F}_4$) generates only repulsive potential energy curves, some of which are of $\Omega=1_u$, 1_g , 4_g , 5_g , and 6_g symmetries, so predissociation of molecules in excited states of these symmetries can occur to this limit while preserving the good quantum numbers. Molecules excited to either $\Omega=0_u^+$ or 0_g^- would not be able to predissociate to the $^3\text{F}_4 + ^3\text{F}_4$ limit, how-

ever, because states of these symmetries are not generated from this limit. Nevertheless, predissociation could occur for molecules excited to these states at the next higher limit, ${}^3F_4+{}^3D_3$, which lies 204.786 cm^{-1} above the ${}^3F_4+{}^3F_4$ limit, and does generate $\Omega=0_u^+$, and 0_g^- repulsive states. All of the bands rotationally resolved near the observed predissociation threshold were $\Omega'=0\leftarrow\Omega''=0$ transitions (see Section III B), strongly suggesting that the observed predissociation threshold corresponds to the ${}^3F_4+{}^3D_3$ limit, and that the $\Omega=1$ levels excited in this energy range are predissociated. Because the ${}^3F_4+{}^3D_3$ separated atom limit lies 204.786 cm^{-1} above the lowest separated atom limit, the predissociation threshold should be corrected by this amount to obtain the bond dissociation energy of Ni₂. The value determined in the present study for the predissociation threshold is $2.067\pm0.002\text{ eV}$, which agrees with the value reported by Morse *et al.*¹⁸ of $2.068\pm0.010\text{ eV}$, resulting in a final value of the Ni₂ bond dissociation energy of $D_0^{\circ}(\text{Ni}_2)=2.042\pm0.002\text{ eV}$.

4. Ionization energy of Ni₂

To determine the ionization energy of Ni₂, the region of $12\,100$ to $14\,400\text{ cm}^{-1}$ was investigated using both ArF excimer radiation (193 nm, 6.42 eV), and Raman shifted ArF radiation (210 nm, 5.90 eV) as the ionization photon in the R2PI experiment. By locating the frequency cutoff where transitions that had been observed with 193 nm radiation for ionization ceased to be observed with 210 nm ionization photons, the adiabatic ionization energy for Ni₂ was determined to be $\text{IE}(\text{Ni}_2)=7.430\pm0.025\text{ eV}$.

The experimental determination of both the bond dissociation energy and the ionization energy of Ni₂ allows the bond strength of the cation, Ni₂⁺, to be obtained by combining this information with the atomic ionization energy, $\text{IE}(\text{Ni})=7.6375\pm0.0012\text{ eV}$,²⁷ through the thermodynamic cycle:

$$D_0^{\circ}(\text{Ni}_2^+)=D_0^{\circ}(\text{Ni}_2)+\text{IE}(\text{Ni})-\text{IE}(\text{Ni}_2). \quad (1)$$

The resulting value for the bond strength of the cation is $D_0^{\circ}(\text{Ni}_2^+)=2.245\pm0.025\text{ eV}$. This value supports the experimental work of Lian *et al.*,²⁸ who determined the bond strength of the cation to be $2.08\pm0.07\text{ eV}$. The small discrepancy between these results may be explained by noting that the experiment of Lian *et al.* was performed using He as the carrier gas in a mild supersonic expansion (reservoir pressure below 1 atm). If the Ni₂⁺ cation is as difficult to cool as the neutral, then the presence of electronically excited cations in the molecular beam would lead to an underestimate of $D_0^{\circ}(\text{Ni}_2^+)$ in the collision-induced dissociation study.

A similar thermochemical cycle relates the bond dissociation energies of Ni₂ and Ni₂⁻:

$$D_0^{\circ}(\text{Ni}_2^-)=D_0^{\circ}(\text{Ni}_2)+\text{EA}(\text{Ni}_2)-\text{EA}(\text{Ni}). \quad (2)$$

Using the electron affinity of Ni₂ as determined by Ho *et al.* [$\text{EA}(\text{Ni}_2)=0.926\pm0.010\text{ eV}$] (Ref. 16) in combination with the revised value of $D_0^{\circ}(\text{Ni}_2)$ and the electron affinity of atomic nickel [$\text{EA}(\text{Ni})=1.156\pm0.010\text{ eV}$] (Ref. 29) this provides a value of $D_0^{\circ}(\text{Ni}_2^-)=1.812\pm0.014\text{ eV}$. Ho *et al.* have assigned the Ni₂⁻ ground state as deriving from the $3d_A^9 3d_B^9 \sigma_g^2 \sigma_u^*$ configuration based on photoelectron spec-

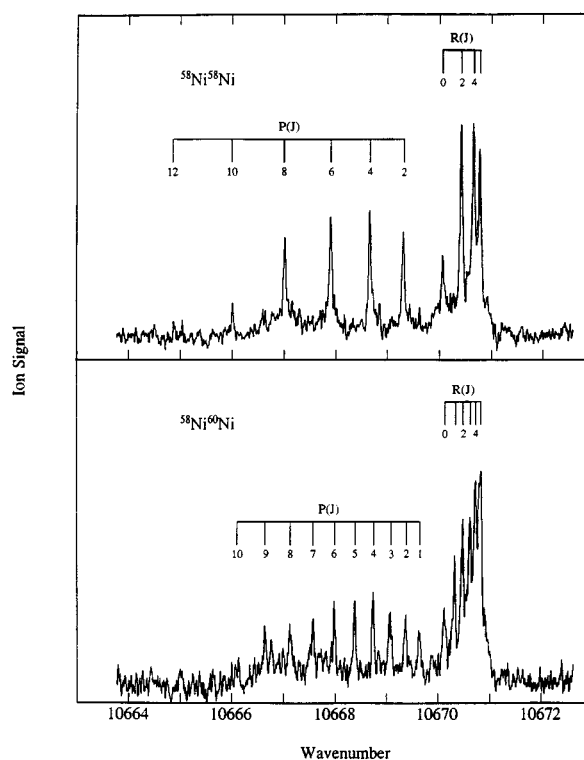


FIG. 4. The rotationally resolved spectrum of the 0-0 band of the $[10.67]0\leftarrow X0$ system for both the homonuclear isotopic (${}^{58}\text{Ni}_2$) and heteronuclear (${}^{58}\text{Ni}{}^{60}\text{Ni}$) modifications of Ni₂.

troscopy.¹⁶ The small reduction in bond strength in moving from Ni₂ to Ni₂⁻ indicates that the σ_u^* orbital in Ni₂⁻ is much more diffuse than in the $3d_A^9({}^2D)3d_B^9({}^3F)\sigma_g^2\sigma_u^*$ states of Ni₂, reducing its antibonding character considerably.

B. Rotationally resolved spectra

Of the 23 bands examined under high resolution using argon as the carrier gas, 20 were successfully analyzed to yield rotational constants and symmetry information in ${}^{58}\text{Ni}_2$. Constants for bands that were assigned to vibronic progressions are reported in Table II. Constants for bands that were not assigned to vibronic progressions, including the $\Omega'=5\leftarrow\Omega''=4$ band observed using helium as the carrier gas, are reported in Table III. The corresponding rotational line positions are available from the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics³⁰ or from the author (M.D.M.). Figure 4 displays the rotationally resolved spectrum of the 0-0 band of the $[10.67]0\leftarrow X0$ system for both the heteronuclear and homonuclear isotopic combinations of Ni₂. The lack of a Q branch is apparent in these spectra, indicating an $\Omega'=0\leftarrow\Omega''=0$ transition. Furthermore, all lines in the ${}^{58}\text{Ni}_2$ spectrum originating from odd J'' levels are missing. Because $I=0$ for ${}^{58}\text{Ni}$, this example of nuclear spin statistics indicates that the transition must originate from an electronic state of either 0_g^+ or 0_u^- symmetry. Unfortunately, our data cannot allow us to distinguish between these two possibilities.

All of the transitions observed using argon carrier gas could be assigned as either $\Omega'=0\leftarrow\Omega''=0$ or $\Omega'=1\leftarrow\Omega''=0$

TABLE II. Rotational analysis of assigned bands of Ni₂.

System	Band	⁵⁸ Ni ₂ ^a	⁵⁸ Ni ⁶⁰ Ni ^a	⁶⁰ Ni ₂ ^a
[9.93]1←X0	1-0	$\nu_0=10\,134.5747(15)$	$\nu_0=10\,133.3279(20)$	$\nu_0=10\,132.0638(15)$
		$B'_1=0.109\,89(10)$	$B'_1=0.108\,09(14)$	$B'_1=0.105\,98(12)$
		$q'_1=-0.000\,187(12)$	$q'_1=-0.000\,170(22)$	$q'_1=-0.000\,111(26)$
		$B''_0=0.125\,31(11)$	$B''_0=0.123\,24(14)$	$B''_0=0.121\,04(11)$
[10.28]1←X0	3-0	$\nu_0=10\,939.8332(75)$	$\nu_0=10\,937.4942(27)$	
		$B'_3=0.108\,50(43)$	$B'_3=0.106\,11(27)$	
		$q'_3=0.000\,227(82)$	$q'_3=0.000\,287(60)$	
		$B''_0=0.125\,68(44)$	$B''_0=0.122\,77(26)$	
[10.67]0←X0	0-0	$B'_e=0.111\,33(10)$	$B'_e=0.108\,94(29)$	
		$\alpha'_e=0.001\,29(09)$	$\alpha'_e=0.000\,98(15)$	
		$r'_e=2.2863(10)\text{Å}$	$r'_e=2.2919(30)\text{Å}$	
		$\nu_0=10\,669.8785(15)$	$\nu_0=10\,669.8935(44)$	$\nu_0=10\,669.9545(33)$
	1-0	$B'_0=0.110\,67(07)$	$B'_0=0.108\,70(26)$	$B'_0=0.107\,37(19)$
		$B''_0=0.125\,42(07)$	$B''_0=0.123\,19(24)$	$B''_0=0.121\,70(20)$
		$\nu_0=10\,901.3482(32)$	$\nu_0=10\,899.4955(28)$	
		$B'_1=0.109\,47(13)$	$B'_1=0.107\,21(19)$	
	2-0	$B''_0=0.125\,23(14)$	$B''_0=0.122\,85(17)$	
		$\nu_0=11\,127.2512(30)$	$\nu_0=11\,123.5785(16)$	
		$B'_2=0.107\,99(21)$	$B'_2=0.106\,60(17)$	
		$B''_0=0.125\,10(19)$	$B''_0=0.122\,99(14)$	
[11.39]1←X0	4-0	$\nu_0=12\,287.1549(29)$		
		$B'_4=0.106\,20(34)$		
		$q'_4=-0.000\,159(63)$		
		$B''_0=0.125\,70(30)$		
[11.90]0←X0	2-0	$\nu_0=12\,314.5776(75)$	$\nu_0=12\,310.1123(52)$	
		$B'_2=0.103\,93(37)$	$B'_2=0.102\,76(39)$	
		$B''_0=0.124\,99(39)$	$B''_0=0.123\,41(35)$	

^aRotational constants and band origins determined by a least-squares fit of the measured line positions to the formula $\nu=\nu_0+(B'\pm q'/2)J'(J'+1)-B''J''(J''+1)$, where the lambda doubling parameter, q' , is only included for $\Omega'=1\leftarrow\Omega''=0$ transitions. Error limits (1σ) are reported following each entry in parentheses.

TABLE III. Rotational analysis of absorption bands of Ni₂.

$\Omega'\leftarrow\Omega''$	⁵⁸ Ni ⁵⁸ Ni ^a			⁵⁸ Ni ⁶⁰ Ni ^a		
	ν_0	B'_v	B''_v	ν_0	B'_v	B''_v
5←4 ^b	11 523.0150(75)	0.108 70 (44)	0.120 33 (49)			
1←0 ^c	12 832.2859(49)	0.101 84 (42)	0.124 80 (45)			
0←0	12 925.9341(37)	0.100 94 (45)	0.124 78 (35)	12 917.2273(42)	0.098 24(41)	0.122 89 (53)
0←0	16 337.7704(20)	0.088 21 (16)	0.125 37 (15)	16 335.9933(33)	0.076 21(29)	0.123 89 (35)
0←0	16 345.4484(60)	0.085 61 (34)	0.126 52 (37)			
0←0	16 347.7823(88)	0.081 41(101)	0.124 01(131)			
0←0	16 362.1650(25)	0.084 18 (24)	0.124 86 (20)			
0←0	16 377.0016(33)	0.087 30 (23)	0.125 56 (26)			
0←0	16 438.5791(77)	0.086 78 (44)	0.125 64 (47)			
0←0	16 471.8397(18)	0.084 14 (17)	0.125 55 (14)			
0←0 ^d				16 473.4084(24)	0.082 22(19)	0.123 51 (21)
0←0	16 477.5667(68)	0.080 12 (47)	0.125 52 (43)			
0←0 ^d				16 479.1672(65)	0.084 68(72)	0.123 67(100)
0←0	16 479.3250(82)	0.084 03 (58)	0.126 15 (52)			
0←0	16 487.2872(40)	0.070 51 (28)	0.125 48 (25)			
0←0	16 496.8736(71)	0.080 89 (40)	0.125 48 (44)			

^aRotational constants and band origins determined by a least-squares fit of the measured line positions to the formula $\nu=\nu_0+(B'\pm q'/2)J'(J'+1)-B''J''(J''+1)$, where the lambda doubling parameter, q' , is only included for the $\Omega'=1\leftarrow\Omega''=0$ transition. Error limits (1σ) are reported following each entry in parentheses.

^bThis band was recorded using helium carrier gas; it disappeared entirely when argon carrier gas was used.

^c $q'=-0.000\,347(122)\text{cm}^{-1}$ for this band.

^dThe spectrum was very congested in this region, and a correlation between bands in the spectra of the different isotopic modifications could not be made with certainty.

transitions, and all displayed this same pattern of missing lines. This identifies the ground state of Ni₂ as either $\Omega=0_g^+$ or 0_u^- , in agreement with theory. The analysis of these bands yields a ground state bond length, r_0 , for ⁵⁸Ni₂ of 2.1545 ± 0.0004 Å, obtained by performing a weighted average of the values found for the individual bands. Similarly, the bond length for ⁵⁸Ni⁶⁰Ni was determined to be 2.1558 ± 0.0006 Å. By comparing the excited state rotational constants in Tables II and III to the ground state rotational constant, it is apparent that the bond is lengthening upon excitation, which is consistent with the *d* electron being promoted from a non-bonding orbital to the σ_u^* antibonding orbital.

IV. DISCUSSION

In the present study improved cooling in the molecular beam has suppressed transitions from $\Omega=4$ lower states that had been previously observed. In addition, the rotational analysis of twenty bands gives us an assignment for the ground state of Ni₂ of either $\Omega=0_g^+$ or $\Omega=0_u^-$. This brings experiment into agreement with both ligand field¹ and *ab initio*³ theoretical studies, which predict two nearly degenerate states of $\Omega=0_g^+$ and $\Omega=0_u^-$ as the lowest molecular states. Because it was not possible to determine the parity of the ground state, however, it has not been possible to identify which of these two possibilities is the true ground state of Ni₂.

An $\Omega=5_u$ state predicted to be either degenerate or nearly degenerate with the $\Omega=0_g^+$ and 0_u^- states was not observed. This state may lie sufficiently high in energy that it was not populated in the molecular beam employing argon carrier gas. However, the number of states that can be accessed by allowed transitions from an $\Omega=5_u$ state is much less than the number that can be accessed from an $\Omega=0_g^+$ or 0_u^- state, so that even if the $\Omega=5_u$ state were populated it is likely that most of the observed transitions would originate from $\Omega=0_g^+$ or 0_u^- . As a result, it is possible that the $\Omega=5_u$ state predicted theoretically is indeed populated in our experiments, but we have simply not resolved any transitions originating from this level.

The bond length determined for the $\Omega=0_g^+$ or 0_u^- ground state, $r_0'' = 2.1545 \pm 0.0004$ Å, is slightly shorter than that found previously for the $\Omega=4$ state (2.200 ± 0.007 Å). Because the $\Omega=4$ state is calculated to be a mix of $\delta\delta$ and $\delta\pi$ *d*-hole states, this implies a lengthening of the bond in the $\delta\pi$ *d*-hole states of Ni₂. It is surprising that the location of the 3*d* hole in the $3d_A^9 3d_B^9 \sigma_g^2$ states of Ni₂ should affect the bond length to this degree, because the 3*d* orbitals are highly contracted in nickel and are not expected to contribute to the bonding. A possible explanation for this effect may be that in the $\delta\pi$ hole states the two positively charged nuclei are not as well shielded from each other as in the $\delta\delta$ hole states, and the additional nuclear repulsion prevents as close an approach. Alternatively, it is possible that a mild heterogeneous perturbation is affecting the excited $\Omega=4$ state of Ni₂, causing its effective rotational constant to be reduced, leading to an erroneous overestimate of its bond length. It is not possible that an analogous erroneous underestimate of the bond length of the ground $\Omega=0_g^+$ or 0_u^- level could be occurring,

for this would require a heterogeneous perturbation of the ground level from below, which is of course impossible.

Comparison of the bond length of Ni₂ (2.1545 Å) to that of the coinage metal analog, Cu₂ (2.2197 Å) (Ref. 31) and to NiCu (2.2346 ± 0.0005 Å) (Ref. 19) is also a bit surprising in that Ni₂ has a similar but shorter bond than Cu₂. One might expect just the opposite, given that the 4*s* orbital of nickel in its $3d^9 4s^1$ configuration is slightly larger than that of copper in its $3d^{10} 4s^1$ configuration. A possible contributor to this difference is that ionic states such as $3d_A^8 3d_B^{10} \sigma_g^2 (\text{Ni}^+ \text{Ni}^-)$ and $3d_A^{10} 3d_B^8 \sigma_g^2 (\text{Ni}^- \text{Ni}^+)$ can contribute via configuration interaction to the Ni₂ ground state, but no corresponding states exist for Cu₂. Regardless of the cause of this effect, it appears not to affect the bond strength of Ni₂ [$D_0^\circ(\text{Ni}_2) = 2.042 \pm 0.002$ eV], which is nearly identical to that of Cu₂ [$D_0^\circ(\text{Cu}_2) = 2.03 \pm 0.02$ eV] (Ref. 31) and NiCu [$D_0^\circ(\text{NiCu}) = 2.05 \pm 0.10$ eV] (Ref. 32). Likewise, the vibrational frequencies of excited states arising from the $3d_A^9(^2D) 3d_B^8(^3F) \sigma_g^2 \sigma_u^*$ manifold in Ni₂ measured in this study (209–234 cm^{−1}) are very similar to the vibrational frequencies of the $3d_{\text{Ni}}^8(^3F) 3d_{\text{Cu}}^{10} \sigma^2 \sigma^*$ manifold in NiCu (192–213 cm^{−1}).¹⁹ All of these similarities are expected in light of the well accepted view that in Ni₂ the bonding is primarily due to the interaction of the 4*s* orbitals.

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