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Electronic ground state of Ni$_2^+$

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The $^4\Phi_{9/2}$ ground state of the Ni$_2^+$ diatomic molecular cation is determined experimentally from temperature and magnetic-field-dependent x-ray magnetic circular dichroism spectroscopy in a cryogenic ion trap, where an electronic and rotational temperature of 7.4 ± 0.2 K was reached by buffer gas cooling of the molecular ion. The contribution of the spin dipole operator to the x-ray magnetic circular dichroism spin sum rule amounts to 7 $T_z = 0.17 ± 0.06 \mu_B$ per atom, approximately 11% of the spin magnetic moment. We find that, in general, homonuclear diatomic molecular cations of 3$d$ transition metals seem to adopt maximum spin magnetic moments in their electronic ground states. Published by AIP Publishing.

I. INTRODUCTION

Homonuclear diatomic molecules and molecular ions have been studied since the first days of quantum mechanics. Surprisingly many of these, in particular those containing transition elements, are still far from being fully understood. Even though they pose a challenge to computational approaches in physics and chemistry, they are studied intensely because of a wide interest in their electronic, magnetic, and catalytic properties.1–10 For example, the nickel diatomic molecular cation Ni$_2^+$ has served as a model system to study the role of surface defects in catalytic activity11 and as one of the smallest systems to study strongly correlated electron phenomena.12 Diatomic molecules of transition elements have also been proposed as systems with large magnetic anisotropy energy.13–15

One prerequisite for large magnetic anisotropy energy is the large orbital angular momentum with significant spin-orbit coupling and strong coupling of the electronic orbital angular momentum to a molecular axis. The spin multiplicity $2S + 1$ and orbital angular momentum projection $\Lambda$ in the ground state of Ni$_2^+$ are, however, not known unambiguously.

A total angular momentum projection of $\Omega = 9/2$ onto the molecular axis and a bond length of 2.225 ± 0.005 Å to 2.242 ± 0.001 Å in the electronic ground state of Ni$_2^+$ were previously determined from rotationally resolved photodissociation spectroscopy.16–19 Reported experimental values of the bond dissociation energy vary from 2.08 ± 0.07 eV to 2.32 ± 0.02 eV, with a preference for the upper values.17,20–21

This experimentally determined $\Omega = 9/2$ ground state is in conflict with theoretical results, which predict $^4\Sigma$ and $^4\Delta$ states or quartet spin states without symmetry specification.22–27

An excited $^3\Gamma$ state is also predicted at ≤ 30 meV above a $^4\Sigma$ ground state.22,23

Here we show that the ground state of Ni$_2^+$ is the $^4\Phi_{9/2}$ state as determined from x-ray magnetic circular dichroism spectroscopy. The assignment agrees in the projected total angular momentum $\Omega = 9/2$ with photodissociation spectroscopy18 and in the quartet spin state with theoretical predictions.22,27

II. EXPERIMENTAL SETUP AND METHODS

The experimental setup has already been described in earlier reports of the electronic ground states of chromium,28,29 manganese,28,30 iron,31 and cobalt31 diatomic molecular cations. As in these previous studies, x-ray magnetic circular dichroism (XMCD) spectroscopy is performed at the Berlin synchrotron radiation facility BESSY II beamline UES2-PGM in a cryogenic linear ion trap that is situated in a $\mu_0H = 5$ T homogeneous magnetic field of a superconducting solenoid.29–36 In brief, Ni$_2^+$ ions are produced by magnetron sputtering of a nickel target with argon ions in helium buffer gas. Cationic species produced in the sputtering and gas-aggregation process are collected at the source exit and transferred by a differentially pumped radio-frequency hexapole ion guide into a quadrupole mass spectrometer.37,38 A continuous and mass-filtered beam of Ni$_2^+$ is then guided into a liquid-helium-cooled quadrupole ion trap and thermalized in the presence of an axial magnetic field by collisions with helium buffer gas at constant pressure in the order of 10$^{-4}$ mbar. Elliptically polarized soft x-ray radiation is coupled into the ion trap with the polarization vector parallel or antiparallel to the magnetic field, and the photon energy is swept across

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the nickel \(L_{2,3} (2p \rightarrow 3d)\) absorption edges from 840.0 eV to 885.8 eV with a photon energy resolution of 400 meV in 0.2 eV steps. Auger decay following core excitation leads to multiply charged diatomic cations, which undergo fragmentation. Product ions eventually resulting from this resonant photoionisation process are collected by the ion trap and mass-analyzed by means of a reflectron time-of-flight mass spectrometer. X-ray absorption and x-ray magnetic circular dichroism spectra were recorded in a partial ion yield mode on the dominant Ni\(^{2+}\) product ion channel. A total of nine data sets were taken under different conditions, yielding XMCD results at eight different ion temperatures and two different magnetic fields. The x-ray absorption and XMCD line shapes agree in all cases, only the XMCD intensity depends on magnetization.

### III. X-RAY MAGNETIC CIRCULAR DICHROISM SPECTROSCOPY OF Ni\(^{2+}\)

The isotropic x-ray absorption spectrum of Ni\(^{+}\), shown in Fig. 1, is taken as the sum of parallel (\(I^+\)) and antiparallel (\(I^-\)) orientation of photon helicity and applied magnetic field. It is in very good agreement with the previously reported linear combination of atomic 3\(d\) states. This is illustrated by computed spectra for a linear combination of atomic 3\(d^8\) 4\(s^2\) and 3\(d^9\) initial state configurations in Fig. 1, calculated in a Hartree-Fock multiplet approach using Cowan’s code as implemented in Missing.

![Fig. 1](https://example.com/figure1.png)

**Fig. 1.** \(L_{2,3}\) edge X-ray absorption and XMCD spectra of Ni\(^{2+}\) recorded at \(\mu_0H = 5\) T applied magnetic field and \(T = 3.8\) K ion trap temperature. The spectral profile of transitions into 3\(d\) derived final states can be reproduced by a combination of 0.35:1 Ni 3\(d^8\) 4\(s^2\) and Ni\(^{+}\) 3\(d^9\) initial states. The smooth increase in the experimental x-ray absorption cross section above 862 eV is due to transitions into higher \(nd\) (\(n \geq 4\)) and \(ns\) (\(n \geq 5\)) derived Rydberg states.

Fig. 1 also shows the XMCD spectrum of Ni\(^{2+}\), i.e., the difference spectrum \(I^- - I^+\), recorded at a magnetic field of \(\mu_0H = 5\) T and 3.8 K ion trap temperature. Because we did not observe a change of the XMCD line shape with magnetization of Ni\(^{2+}\) and because \(I^-\) and \(I^+\) are always positive values, the asymmetry at the \(L_3\) edge varies linearly with magnetization and is limited to \(|(I^- - I^+)/(I^- + I^+)| \leq 1\) in the case of saturation magnetization. It can therefore be used as a relative measure of magnetization, and the absolute value of the XMCD asymmetry at the maximum of the \(L_3\) resonance (\(\approx 852.25\) eV) of \(|(I^- - I^+)/(I^- + I^+)| = 0.58\) indicates a magnetization of \(\geq 0.58\) times the total magnetic moment of Ni\(^{2+}\).

At the same time, the large negative XMCD signal at the \(L_3\) edge and the small but again negative XMCD signal at the \(L_2\) edge, visible as a step in the integrated XMCD spectrum, indicate significant orbital magnetization and thus a large orbital contribution to the total magnetic moment. Application of the XMCD orbital and effective spin sum rules\(^{33,44}\) to the spectrum in Fig. 1, recorded at lowest temperature of the ion trap and highest applied magnetic field, yields orbital and effective spin magnetizations, \(m_\Lambda\) and \(m_\Sigma\), per unoccupied 3\(d\)-derived state of \(m_\Lambda = 0.64 \pm 0.01\) \(\mu_B\) and \(m_\Sigma = 0.72 \pm 0.10\) \(\mu_B\).

### IV. ELECTRONIC GROUND STATE OF Ni\(^{2+}\)

#### A. Electronic configuration and candidate states

The lowest-energy asymptote of Ni\(^{2+}\) in the limit of separated atoms corresponds to Ni 3\(d^8\) 4\(s^2\) 3\(F_4\) + Ni\(^+\) 3\(d^9\) 2\(D_5/2\) and leads to a 3\(d^{17}\) 4\(s^2\) electronic configuration of the diatomic molecular cation. Only 25 meV higher in energy is the Ni 3\(d^8\) 4\(s^1\) 3\(D_3\) + Ni\(^+\) 3\(d^9\) 2\(D_3/2\) asymptote that would lead to a 3\(d^{18}\) 4\(s^1\) electronic configuration. Averaging over spin-orbit coupled states inverts the energetic order and places the latter asymptote 30 meV below the former.\(^{30,45}\) We therefore consider both asymptotes in the following, even though the experimental x-ray absorption and XMCD spectra already indicate a contribution of atomic 3\(d^9\) and 3\(d^8\) configurations, making the 3\(d^{18}\) 4\(s^1\) configuration less likely the one that correctly describes Ni\(^{2+}\). Both asymptotes limit the spin multiplicity of Ni\(^{2+}\) to 2\(S + 1\) \(\geq 2\), and the projection \(\Lambda\) of the orbital angular momentum onto the molecular axis is limited to \(\Lambda \leq 5\) for the 3\(d^{17}\) configuration and \(\Lambda \leq 4\) for the 3\(d^{18}\) molecular configuration.

#### B. Analysis of the orbital magnetization

XMCD sum rules\(^{33,44}\) link the integrated intensities at the \(L_3\) and \(L_2\) edges of the XMCD asymmetry, depicted in the lower panel of Fig. 1, to expectation values \(\langle L_z \rangle\) and \(\langle S_z \rangle + 7/2\langle T_z \rangle\) of the orbital and spin angular momenta, where \(T_z\) is the intra-atomic spin dipole operator\(^{46-50}\) that contributes to the XMCD effective spin sum rule. These expectation values are connected to magnetizations by \(m_\Lambda = \mu_B\langle L_z \rangle\) and \(m_\Sigma = m_T + \mu_B\langle L_z \rangle\) \((\langle S_z \rangle + 7/2\langle T_z \rangle\)) of the orbital angular momentum sum rule\(^{15}\) of XMCD is more robust than the effective spin sum rule\(^{44}\) because the former does not suffer from \(T_z\) contributions nor does it require a separation of \(L_1\) and \(L_2\) transitions in the experimental spectra.\(^{51}\) Furthermore, the spin magnetic moment of Ni\(^{2+}\) might not be purely 3\(d\) derived but could have
additional contributions from 4s or orbitals, which $L_{2,3,4}$-edge XMCSD is insensitive to. In contrast, only 3d derived $\pi$ and $\delta$ orbitals contribute to the orbital angular momentum of Ni$_2^+$. As a first step, we therefore use the detected orbital magnetization $m_d$ as a measure of the hypothetical total magnetization of Ni$_2^+$ for each of the candidate electronic states. This is done by multiplying the highest experimental orbital magnetization obtained in the series of temperature and field-dependent XMCSD spectra, $m_d = 0.64 \pm 0.01 \mu_B$ per unoccupied 3d state, with the number of unoccupied 3d states for the possible 3d$^{17}$ 4s$^2$ ($m_d = 1.92 \pm 0.03 \mu_B$) and 3d$^{18}$ 4s$^1$ ($m_d = 1.28 \pm 0.02 \mu_B$) configurations of Ni$_2^+$. These values are then normalized to the projected orbital magnetic moments $\Lambda$ of each candidate electronic state of the corresponding configurations. We compare the values of $m_d/\Lambda$ thus obtained for the different candidate states to the condition of $0.58 \leq m_d/\Lambda \leq 1$, where the lower limit of the relative magnetization is set by the XMCD asymmetry under the same experimental conditions, and the upper limit is set by saturation magnetization.

This analysis shows that $H$ ($\Lambda = 5$) and $\Gamma$ ($\Lambda = 4$) states of the 3d$^{17}$ 4s$^2$ configuration as well as $\Gamma$ ($\Lambda = 4$) and $\Phi$ ($\Lambda = 3$) states of the 3d$^{18}$ 4s$^1$ configuration are incompatible with the condition of a relative magnetization of $\geq 0.58$ derived from the XMCD asymmetry at the $L_3$ edge. These states can therefore be ruled out. Likewise, all $\Pi$ ($\Lambda = 1$) and $\Sigma$ ($\Lambda = 0$) states can be ruled out because the absolute value of the orbital magnetization cannot become larger than the orbital magnetic moment. Thus, without any further assumptions, the detected orbital magnetization and the limits of $1.92 \pm 0.03 \leq \Lambda \leq 3.31 \pm 0.05$ for the 3d$^{17}$ 4s$^2$ configuration as well as $1.28 \pm 0.02 \leq \Lambda \leq 2.21 \pm 0.03$ for the 3d$^{18}$ 4s$^1$ configuration only allow $\Delta$ ($\Lambda = 2$) and $\Phi$ ($\Lambda = 3$) states for the 3d$^{17}$ 4s$^2$ configuration and $\Lambda$ ($\Lambda = 2$) states for the 3d$^{18}$ 4s$^1$ configuration.

C. Ion temperature considerations

The ion temperatures that would correspond to these electronic states of the rotating Ni$_2^+$ molecular ion in the applied magnetic field are obtained by numerically solving an effective Zeeman Hamiltonian$^{52,53}$ at the respective magnetizations for Hund’s case (a) angular momentum coupling.$^{31}$ We use the experimental value of $2.225 \pm 0.001$ Å of the equilibrium distance$^{10}$ to determine the rotational constant that is a necessary parameter. The ion temperature allows us to further exclude $\Delta$ ($\Lambda = 2$) states of the 3d$^{17}$ 4s$^2$ configuration because these would correspond to ion temperatures of $\leq 1$ K, i.e., significantly lower than the lowest ion trap temperature of 3.8 K. At this stage, only $\Phi$ ($\Lambda = 3$) states of the 3d$^{17}$ 4s$^2$ configuration and $\Delta$ ($\Lambda = 2$) states of the 3d$^{18}$ 4s$^1$ configuration are left as potential candidates for the electronic ground state of Ni$_2^+$.

While the spin multiplicity could be 2 or 4 in both cases, only 3d derived electronic spins contribute to the multiplicity for the 3d$^{17}$ 4s$^2$ configuration but also a 4s derived spin contributes in case of the 3d$^{18}$ 4s$^1$ configuration. This single spin in the singly occupied 4s or molecular orbital could be coupled parallel or antiparallel to the 3d-derived spins, giving rise to 3d$^{17}$ ($^3\Delta$) 4s$^1$ $^2\Delta$ and 3d$^{18}$ ($^3\Delta$) 4s$^1$ $^4\Delta$ states. The 3d$^{18}$ ($^3\Delta$) 4s$^1$ $^2\Delta$ state with antiparallel spin coupling of the 3d and 4s derived states would correspond to an ion temperature of $3.4 \pm 0.4$ K, just below the ion trap temperature of 3.8 K, and can also be ruled out because of inevitable radio-frequency heating of the ions. Another possible state, 3d$^{18}$ ($^1\Delta$) 4s$^1$ $^2\Delta$, with an equal number of occupied 3d derived spin-up and spin-down states can also be ruled out because this state would lead to a vanishing 3d spin magnetization, in contradiction to the experimental finding of $m_z = 0.72 \pm 0.10 \mu_B$ per unoccupied 3d derived state. This reduces the remaining candidate states to $^2\Phi$ and $^4\Phi$ for the 3d$^{17}$ 4s$^2$ configuration and $^4\Delta$ for the 3d$^{18}$ 4s$^1$ configuration.

D. Analysis of the ratio of orbital-to-spin magnetization

These remaining candidate states are assessed by the experimentally determined ratio of orbital-to-spin magnetization of Ni$_2^+$, which is equal to the ratio of orbital-to-spin magnetic moments in Hund’s case (a) coupling of the angular momenta. This ratio of orbital to effective spin magnetic moment $\mu_d/\mu_z$ of Ni$_2^+$ is shown as a function of the orbital magnetization $m_d$ per 3d hole in Fig. 2, obtained by the sum rule analysis of a series of temperature and magnetic-field-dependent XMCSD spectra of Ni$_2^+$. Except for the lowest magnetization, which was recorded at $\mu_0H = 1.19$ T, these data were obtained at $\mu_0H = 5$ T for different temperatures of the trapped ions by variations of buffer gas pressure, radio-frequency amplitude, and ion trap temperature. A weighted linear fit of $\mu_d/\mu_z$ yields an intercept of $0.86 \pm 0.12$ and a slope of $0.05 \pm 0.16$, i.e., zero slope within the error bars. Since a constant ratio is indeed expected in LS coupling,$^{22,34}$ the ratio of $\mu_d/\mu_z$ can be given as $0.90 \pm 0.03$ from a weighted average that is shown as a dashed line in Fig. 2.

For the remaining states of the 3d$^{17}$ 4s$^2$ configuration, values of $\mu_d/\mu_z = 3$ for the $^2\Phi$ state and $\mu_d/\mu_z = 1$ for the $^4\Phi$ state would be expected. For the $^4\Delta$ state of the 3d$^{18}$ 4s$^1$ configuration, only the $^3\Delta$ contribution of the 3d derived subshell with a value of $\mu_d/\mu_z = 1$ can be compared with the experimental ratio to which the 4s derived spin does not contribute. As can be seen, none of the remaining candidate states has a value of $\mu_d/\mu_z$ that directly falls within the

![FIG. 2. Experimental ratio of Ni$_2^+$ orbital-to-spin magnetic moments as a function of the orbital magnetization, which was varied by ion temperature at constant $\mu_0H = 5$ T. Only the value for the lowest orbital magnetization was obtained at $\mu_0H = 1.19$ T. Ion temperatures that correspond to the $^4\Delta$ ground state are indicated in the upper axis for comparison.](image-url)
The electronic ground state of the Ni$^+$ diatomic molecular cation is determined as $^4\text{Do}^{12}$ from x-ray magnetic circular dichroism spectroscopy of cryogenic ions in a linear ion trap. This ground state of Ni$^+$ agrees in the total angular momentum projection $\Omega = 9/2$ with previous experimental results, and in the spin multiplicity $2S + 1 = 4$ with theoretical predictions. Ni$^+$ is a further example of a homonuclear diatomic molecular cation of 3$d$ transition elements that adopts the maximum spin multiplicity, significant orbital angular momentum, and small spin-dipole term in its ground state.

VI. CONCLUSION

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