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Rotationally resolved magnetic vibrational circular dichroism of the paramagnetic molecule NO[†]

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Magnetic vibrational circular dichroism (MVCD) enables the measurement of molecular magnetic moments with modest spectral resolution. Due to its paramagnetism, NO gives a much stronger spectral response, about 3 orders of magnitude more intense, than do typical diamagnetic molecules. The molecule thus provides a convenient test for the experiment and theory of paramagnetic rotors. We have measured and analyzed the MVCD, equivalent to the molecular Zeeman spectra, of NO in co-linear magnetic fields of 0.1, 0.2, 2, 4 and 8 Tesla. Similar MVCD intensities were observed for both the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components of NO, particularly for high J values, which demonstrates a considerable deviation from pure Hund's case (a) for NO. The g_J-values for the ${}^{2}\Pi_{1/2}$ components of NO, which can be determined from our experimental spectra by moment analysis, agree well with the predicted values from Radford's theory. For the ${}^{2}\Pi_{3/2}$ components, we tested this theory by simulating the MVCD and absorption spectra, and comparing them with our experimental spectra by use of moment analysis to show that they match well in terms of magnetic properties. While 0.2 T experiments easily develop sufficient MVCD for analysis of NO spectra and these low field intensities have a linear field dependence, spectra in the strong fields accessible in our study showed non-linear response due to onset of saturation effects. We also observed a strong field dependence for the absorption intensities for some ${}^{2}\Pi_{3/2}$ components that was not encompassed in the theoretical model. Finally, a full coupling scheme provided analytical MVCD and absorption intensities that were in good agreement with the experimental values.

Introduction

Previous magnetic vibrational circular dichroism (MVCD) studies have been focused on diamagnetic molecules which include several related series of high symmetry polyatomic molecules in the condensed phase^{1–8} and some small gas phase molecules for which rotationally resolved spectra could be obtained.^{9–11} Although the molecular Zeeman effect is generally quite small, the rotational components of dipole allowed vibrational transitions that are, in particular, measurable with the MVCD technique using moderately high magnetic fields, even with a spectrometer of relatively modest resolution. This polarization modulation (intensity based measurement) detection method under steady state field perturbation transduces the small Zeeman energy splitting into a substantial MVCD intensity difference which yields a characteristic pattern. From another

^a Hinds Instruments, Inc., 7245 NW Evergreen Pkwy., Hillsboro, OR 97124, USA point of view, optical activity measured for gas phase molecules has attracted attention for studies in both the electronic^{12,13} and vibrational regions,^{14,15} as it allows access to isolated molecules and enables one to benchmark accurate computations and theories.¹⁶

However, in the case of NO, a paramagnetic diatomic splitting of the absorption band (for the Q branch) is observable at modest resolution as well. By comparing the lowest and highest fields, we could follow how the splitting of the energy levels changes and is further magnified with MVCD. NO is one of the most intensively studied diatomic molecules with the Zeeman effect because of the complexities that arise from coupling the electronic orbital, spin and molecular rotational angular momenta.^{17–19} In terms of modulation spectroscopy, different techniques have been developed to study the Zeeman effect of NO. Herrmann et al.^{20,21} utilized a tunable IR laser with right and left circular polarizations and a small modulated magnetic field. Guelachvili applied both a modulating and a constant field with a very high resolution FTIR but initially used no polarizing optics.^{22,23} Later, he and his coworkers also used polarization modulation of the high resolution Fourier transform spectra for NO detection.²⁴ In this latter experiment, a quarter wave plate and a rotating polarizer were placed before the interferometer to achieve polarization modulation.

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Most recently, NO spectroscopy and Zeeman effects have attracted considerable interest from a sensitive detection point of view, due to the biological and environmental impact of NO. Tunable diode laser absorption spectra (TDLAS) are of very high resolution and additionally have been improved by developments with QCL (quantum cascade laser) light sources, as was reviewed in an alternate study using modulated *B* fields of ~100 G and a UV diode for electronic transitions.²⁵ Instead of tuning the light source to match the transitions, coincidence of NO Zeeman lines and CO laser lines achieved by varying the magnetic field can be used for detection purposes. These various laser methods have allowed detection of N₂ isotopes (*via* NO transitions),²⁶ NO in breath,^{27,28} and in the atmosphere.^{21,29}

NO is also interesting in terms of its spectra not fitting either Hund's coupling case (a) or (b). It is a stable paramagnetic molecule and the coupling case for the electronic and spin angular momenta was early on proposed to be close to Hund's case (a).³⁰ Formulas for the coupling and energy levels have been worked out^{31,32} and have recently been revised in studies interpreting the Zeeman shifts detected with CO laser coincidence.³³ As is well known, molecular Zeeman g_J -factors in pure Hund's coupling case (a) would be $g_I \sim 0$ (effectively non-magnetic) and $g_J = 3/J(J + 1)$ for the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ states, respectively.^{30,34} However, the Zeeman effect for the ${}^{2}\Pi_{1/2}$ state of NO was in fact observed as early as 1955 in a magnetic field as low as 100 G using mm wave techniques.³⁵ The theoretical treatment of the Zeeman effect for ${}^{2}\Pi$ states of light diatomic radicals has been extended by Radford¹⁷⁻¹⁹ to a general intermediate coupling case between Hund's (a) and (b) to explain magnetic resonance spectra (using EPR methods).

Here we report the experimental and simulated MVCD and infrared absorption spectra for NO. Our results add evidence for a considerable deviation from Hund's case (a) for NO and provide a more general test for Radford's theory than previously available, because we can simulate and measure spectra for a large number of *J*-values in both the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components of NO. Additionally we have found a large non-linearity at high fields, which reflects other such determinations for selected NO Zeeman transitions using CO laser sources.^{33,36} Those experiments used high resolution laser lines to match selected Zeeman shifted lines with variation of the field in a damped oscillation. Although our approach uses simple static fields, a modest resolution FTIR, and samples all the transitions, the effects of non-linearity are still quite evident with MVCD for selected transitions.

Methods

MVCD measurement

In our MVCD experiment, we modulate the circularity of the light polarization and maintain a constant magnetic field. By using a superconducting magnet, we can easily maintain constant field strengths from 0.1 to 8 Tesla. The stronger fields had previously been needed for the study of the rotational and vibrational Zeeman effect of diamagnetic molecules to achieve a measurable intensity modulation correlated to the energy splitting.

By contrast, for the paramagnetic NO molecule, only a low field (100's of Gauss) is needed to observe the modulation signal with Zeeman modulation techniques.^{20–24} Consequently, most studies on the Zeeman effect of NO have been done using magnetic fields, below 1 Tesla, but with high resolution spectral techniques. Since MVCD for NO can be measured with a broad range of the magnetic field strengths, we also tested the linearity of the MVCD and IR spectral dependence on the applied field.

MVCD spectra were measured using an experimental set-up that has been described elsewhere in detail^{7,8,37–39} and which consists of a Fourier transform IR (Digilab FTS-60), coupled to an external MVCD bench containing polarization optics and an up to 8 Tesla (at 4.2 K) horizontal bore, superconducting magnet (Oxford Instruments). For near-IR MVCD, a BaF₂ substrate Al grid polarizer (Cambridge Physical Sciences) and a CaF₂ modulator (Model PEM 80-II, Hinds International) were placed before the sample to modulate the circular polarization at 57 kHz. After the sample, the light was focused with a CaF₂ lens onto a high D* Hg(Cd)Te detector (Infrared Associates).

NO was obtained from Matheson (CP) and was used, without further purification, by expansion at a pressure of about 10 Torr into a homemade 5 cm path length sample cell, sealed with KBr windows. This is held in a brass cylinder that incorporates a fill valve and is designed to fit centered in the most homogeneous part of the field in the magnet bore.

MVCD spectra were run at five different magnetic field strengths: ± 0.1 , ± 0.2 , ± 2 , ± 4 and ± 8 Tesla. By changing the orientation of the field and subtracting the two resulting spectra, any baseline irregularities (CD offsets) were corrected. The modulated spectra at each field were obtained, at a nominal 0.5 cm⁻¹ resolution, by averaging over two blocks of 1024, 512, 64, 32 and 16 scans, respectively, and normalizing to the single-beam transmission spectra. The final MVCD spectra were the difference of the positive and negative field spectra scaled for intensity calibration^{37–41} and corrected for the actual magnetic field used. In contrast to previous reports,^{9–11} the MVCD spectra in the figures are not field normalized in order to illustrate better the effects of varying the magnetic field.

Experimental results

The experimental absorption and MVCD spectra at 0.2 and 2 Tesla are plotted in Fig. 1 and 2, respectively, for the entire



Fig. 1 Experimental absorption and MVCD of NO at 0.2 T, for pressure 10 Torr, resolution 0.5 cm^{-1} , 1024 scans averaged at $\pm 0.2 \text{ T}$, and subtracted.



Fig. 2 Experimental absorption and MVCD of NO at 2 T. Measured as in Fig. 1, but 256 scans averaged.

ro-vibrational band accessible at room temperature. The overall magnitudes of the MVCD signals in this spectrum, in terms of $\Delta A/A$ values at the same field strength, are about 3 orders of magnitude higher than what is found for rotationally resolved MVCD of diamagnetic molecules.^{9–11} Many absorption and MVCD features are common for the spectra measured at different magnetic field strengths. With 0.5 cm⁻¹ resolution, there is overlap and cancellation in the individual Zeeman component absorption and MVCD spectra, but the ²Π_{1/2} and ²Π_{3/2} transitions for each J^{9–11} are resolved for relatively high J-value transitions in both *P*- and *R*-branches. Each of the absorption peaks appearing in our spectra contains two unresolved A-doubling components.

The Zeeman interaction of the magnetic moment correlated to the total angular momentum leads to MVCD of individual *J*-levels being dominated by overlapping *A* terms (derivative shapes) of opposite sign for the higher *J*-value ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ ro-vibrational transitions.⁴² At low *J*-values, there is initially dominance by the ${}^{2}\Pi_{3/2}$ transitions, and then cancellation in the overlapped spectra as the *g*-value for the ${}^{2}\Pi_{3/2}$ state changes sign. As the transitions for the two states become resolved, the oppositely signed *g*-values become evident due to the oppositely signed *A*-term band shapes indicative of two separate first order Zeeman effects.

All the MVCD spectra measured at five different fields, in both the *P*- and *R*-branches, show these oppositely signed *A*-term patterns for the higher *J*-value ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components, *i.e.*, ${}^{2}\Pi_{1/2}$ -positive and ${}^{2}\Pi_{3/2}$ -negative. The ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components also have similar MVCD intensity, in terms of $\Delta A/A$, in both the *P*- and *R*-branches for high *J*-values. While at higher *J*-values the two *A*-terms become effectively resolved, for the lowest *J*-value transitions the experimental MVCD spectra become distorted, particularly for the *R*-branch.

The MVCD and the absorption features do demonstrate some variation as the field is changed. For the low field spectra, $\Delta A/A$ values of 0.15 and 0.30 were obtained for the *Q*-branch at 0.1 and 0.2 Tesla, respectively, indicating a linear field dependence, while MVCD *A*-terms, at least 10 times weaker, were seen in both *P*- and *R*-branches. However, with increasing field, the *Q*-branch splits and the MVCD does not grow in intensity but the *P*- and *R*-branch MVCD do, as illustrated in Fig. 3 for the unresolved *Q*-branch and the *P*(3/2) and *R*(1/2) transitions at 0.1, 0.2, 2, 4 and 8 Tesla. The irregular band shape for the *Q*-branch absorption and MVCD



Fig. 3 Field dependence of the absorption (left) and MVCD (right) for NO in *Q* branch plus P(3/2) and R(1/2) bands at 0.1, 0.2, 2, 4, 8 T, from bottom to top.

spectra results from overlap of the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components and their resolvable splittings at high field are due to the comparatively large Zeeman effect in NO. On the other hand, the Zeeman splitting of the *Q*-branch becomes evident at high fields even in absorption alone.

The quantitative changes in the *P*- and *R*-branches of the absorption and MVCD spectra as the magnetic field strength is increased from 0.1 to 8 Tesla also show unusual intensity effects and significant non-linearity. Selected examples of transitions from the *P*- and *R*-branch absorption and MVCD spectra that have maximal field effects are shown in Fig. 4. For both branches, the ${}^{2}\Pi_{1/2}$ component shows no obvious change in absorption for different field strengths under our experimental conditions, but the ${}^{2}\Pi_{3/2}$ component shows an intensity increase with increasing field. Additionally, the MVCD for 8 T is only marginally stronger than that for 4 T, showing the loss of linearity.

The MVCD signals should increase linearly with increasing field strength in the absence of saturation.²⁰ In terms of $\Delta A/A$, the MVCD is linearly dependent on field strength for low ΔA values which occur at low fields (below 0.2 Tesla). This can be seen by the MVCD intensity observed at 0.2 Tesla being exactly double that obtained at 0.1 Tesla while the absorption shows no observable change. However, the MVCD is obviously saturated at 8 Tesla, where the ΔA values become as large as 0.4, as can be easily recognized from comparison of the 4 and 8 Tesla results in Fig. 4.

Simulations

The simulation of the rotationally resolved MVCD spectra is based on the theory of rotational states of molecules in the ${}^{2}\Pi$ state, as described elsewhere.^{43,44} For clarification of our approach to spectral simulation, we provide here a brief summary of the formulae used for the energy levels and transition intensities.

The ² Π molecules have S = 1/2 spin and L = 1 electronic orbital angular momenta. In the case of NO, the total angular momentum vector F is a sum of individual contributions:

$$\boldsymbol{F} = \boldsymbol{J} + \boldsymbol{I} = \boldsymbol{R} + \boldsymbol{S} + \boldsymbol{L} + \boldsymbol{I}, \tag{1}$$



Fig. 4 Nonlinearity of MVCD and field dependent absorbance (for the ${}^{2}\Pi_{3/2}$ component) in selected *P* (left) and *R* (right) branch transitions for NO. Measured as in Fig. 1 for fields of 0.1, 0.2, 2, 4, and 8 T.

where R, S, L and I denote the rotational, spin, electronic orbital and nuclear angular momentum, respectively.

We develop here only the equation for even parity states $({}^{2}\Pi^{+})$, since odd parity $({}^{2}\Pi^{-})$ states give nearly the same energy levels.⁴³ As a basis set, the following functions were taken:

$$\Pi_{1/2} = \frac{1}{\sqrt{2}} \left(|n1\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle \left| J \frac{1}{2} M \right\rangle + |n-1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle \left| J - \frac{1}{2} M \right\rangle \right)$$
(2a)

$$\Pi_{3/2} = \frac{1}{\sqrt{2}} \left(|n1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle \left| J \frac{3}{2} M \right\rangle + |n-1\rangle \left| \frac{1}{2} - \frac{1}{2} \right\rangle \left| J - \frac{3}{2} M \right\rangle \right).$$
(2b)

For these rovibronic wavefunctions we used the notation (Hund's case (a) wavefunctions):

$$|n\Lambda\rangle|S\Sigma\rangle|J\Omega M\rangle,$$
 (3)

where *n* denotes the vibrational and electronic state, Λ is the projection of the electronic angular momentum L on the molecular axis, S and Σ are the spin and its projection on the molecular axis, respectively, J is defined in eqn (1), Ω is the projection of J (and also L + S) on the molecular axis, M is the projection of J on a space-fixed axis.

Without any perturbation the energies of two eigenstates are determined by spin–orbital coupling:

$$E_{\pm} = B_{\nu} \left[\left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right) \pm \frac{X}{2} \right], \tag{4}$$

$$g_F = \frac{g_J[F(F+1) + J(J+1) - I(I+1)] + g_I[F(F+1) + I(I+1) - J(J+1)]}{2F(F+1)}.$$
(8)

where $X = \sqrt{4(J - 1/2)(J + 3/2) + (Y - 2)^2}$, $Y = A_v/B_v$; A_v and B_v are the spin-orbit coupling and rotational constants, respectively (Table S1, ESI†), v is the vibrational quantum number. The eigenstates are:

$$|JM_{J}\rangle_{+} = \psi(F_{2}) = \psi_{1/2} = a|\Pi_{1/2}\rangle + b|\Pi_{3/2}\rangle$$
 (5a)

$$|JM_{J}\rangle_{-} = \psi(F_{1}) = \psi_{3/2} = -a|\Pi_{1/2}\rangle + b|\Pi_{3/2}\rangle,$$
 (5b)

where $a = (X + Y - 2)^{1/2} (2X)^{-1/2}$ and $b = (X - Y + 2)^{1/2} (2X)^{-1/2}$. As indicated in (eqn (5a) and (b)), the + sign in eqn (4) produces so called " F_2 " states (and the – sign leads to "F1" states).^{24,25} The ground state is close to Hund's $\Pi_{1/2}$ state for low Js.

For MVCD, we need to further consider the loss of degeneracy of the rotational levels caused by the magnetic field. We do that for the total molecular wavefunction (including the nuclear momentum) obtained from the uncoupled wavefunctions as

$$|FM_F\rangle = \sum_{M_J} \sum_{M_I = M_F - M_J} \langle J, M_J, I, M_I | F, M_F \rangle |J M_J I M_I \rangle, \quad (6)$$

where $\langle J, M_J, I, M_I | F, M_F \rangle$ is the Clebsch–Gordan coefficient, and $|J M_J I M_I \rangle = |J M_J \rangle |I M_I \rangle$ is a product of **J** and **I** angular momentum functions.

If a magnetic field, B, is present, the molecular energy E is

$$E = E_{\pm} + g_F M_F \mathbf{B}_Z \mu_{\mathbf{B}}, \tag{7}$$

where M_F is the projection of F on the direction B_Z of the magnetic field intensity, and μ_B is the Bohr-magneton.

The molecular magnetic moment is $\mathbf{m} = \mu_{\rm B}g_F \mathbf{F} = \mu_{\rm B}g_J \mathbf{J} + \mu_{\rm B}g_I \mathbf{I}$, in units of Bohr magneton, so that the "g-factors" are dimensionless. Therefore $g_F \mathbf{F}^2 = g_J \mathbf{J} \cdot \mathbf{F} + g_I \mathbf{I} \cdot \mathbf{F}$. Using $\mathbf{J} \cdot \mathbf{F} = (\mathbf{F}^2 + \mathbf{J}^2 - \mathbf{I}^2)/2$ and $\mathbf{I} \cdot \mathbf{F} = (\mathbf{F}^2 + \mathbf{I}^2 - \mathbf{J}^2)/2$, we get the g_F factor for the coupled representation as

Note, that for high J, $g_F \approx g_J$. For this paramagnetic molecule, the nuclear g-factor, g_I , is much smaller than g_J and will be neglected.

The J g-factor is dependent on J as:^{17,20}

$$g_J = g(J) = \frac{3/2 \pm [2(J-1/2)(J+3/2) - 3Y/2 + 3]/X}{J(J+1)}.$$
 (9)

The plus sign is applied for the F_2 state.



Fig. 5 Simulated absorption (ε) and MVCD ($\Delta \varepsilon$) spectra for NO at 2 T using a 0.3 cm⁻¹ line width for summing computed components.

The spectral intensities were calculated *via* evaluation of the matrix elements of the electric dipole moment operators between ground and excited ro-vibrational states $\langle g | \mu_{\pm} | e \rangle$ for each transition, $g \rightarrow e$, as defined by Stephens, using the Wigner–Eckart theorem.^{9,42,43,45} The line strength for a transition $|FM_F\rangle(J) \rightarrow |F'M'_F\rangle(J')$ for left and right CPL can thus be calculated using Clebsch–Gordan coefficients⁴³ and the Wigner three-*j* symbols⁴³ as:

$$A_{L/R} = \omega \mu^2 (2J+1)(2J'+1)[\langle J, M_J, 1, M_F - M_J | F M_F \rangle$$

$$\langle J', M_J + 1, 1, M'_F - M_J - 1 | F' M'_F \rangle$$

$$\begin{pmatrix} J' & 1 & J \\ -M_J - 1 & \pm 1 & M_J \end{pmatrix} f_0^{2} \exp(-E/kT)$$
(10)

where

$$f_0 = a_g a_e \begin{pmatrix} J' & 1 & J \\ -1/2 & 0 & 1/2 \end{pmatrix} - b_g b_e \begin{pmatrix} J' & 1 & J \\ -3/2 & 0 & 3/2 \end{pmatrix},$$
(11)

 ω is the transition frequency, μ the transition dipole moment, and $\exp(-E/kT)$ is the usual Boltzmann population weighting.

Parameters used for the simulation are given in Table S1 (ESI[†]). MVCD and absorption spectra simulated for 2 Tesla are shown in Fig. 5. The spectral band shapes were simulated by summing individual components, each assigned a Gaussian shape with a 0.3 cm⁻¹ bandwidth and weighted by the computed line strengths.

Discussion

By using an intense constant magnetic field with polarization modulation to detect its effect on intensities, MVCD has higher sensitivity to the Zeeman effect than do field modulation techniques. Furthermore, such fixed fields used with polarization modulation detection are easier to calibrate to obtain quantitative measures of the *g*-values. We can easily maintain a magnetic field of 8 Tesla while a typical modulating field is limited to the order of a few hundred Gauss.^{20–24} This advantage is quite important when the Zeeman splitting is small as is usually found for diamagnetic molecules^{9–11} which have magnetic moments of the order of the nuclear magneton in contrast to NO which has magnetic moments of the order of the Bohr magneton. While higher resolution techniques are desirable for measurement of weak molecular perturbations, the MVCD technique provides a simple alternative, allowing facile detection of high resolution spectroscopic phenomena with a low resolution spectrometer.

With the FT method, all transitions are accessed, and the band shape fitting procedure, normalized to the absorbance through moment analysis, provides an alternative to frequency based studies requiring high resolution and selection of those bands that are coincident with the laser line. Of course, resolution can also be increased with the FT method, as done by Guelachvili,²² but the added expense and complications, as well as the much longer data acquisition times, are not required. Nonetheless, with intensity based measurements, the precision will be reduced from that of a laser or ultrahigh resolution FTIR frequency based measurement. In our experiments, the accuracy was not significantly compromised as shown by the excellent agreement with the theoretical model, especially for high J values.

Rapid scan FTIR coupled with high frequency polarization modulation for a sample in a collinear magnetic field is an optimal method for high signal-to-noise ratio Zeeman-effect detection, especially for diamagnetic molecules, and for paramagnets, even more so. For example, the MVCD spectrum shown in Fig. 1 (at only 0.2 T field strength) was collected in less than an hour of spectrometer time, which reflects the high efficiency obtainable using the modest resolution of this MVCD technique. Additionally, with paramagnets like NO, even frequency based Zeeman effects could be detected at higher fields, in the *Q*-branch.

The fact that similar MVCD intensities were observed for the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components in both the *R*- and *P*-branches is qualitatively consistent with the previously reported results^{20,24,35} which demonstrate that NO deviates from a pure Hund's case (a) type molecule. In such Hund's case (a), the Zeeman effect and thus the MVCD intensities for the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ components should be very different, which is obviously inconsistent with our observations. The results show considerable state mixing, as suggested in eqn (5). That the spectra do fit the general predictions of Radford's theory is seen by the overall similarity of the predicted spectra shown in Fig. 5 with those in Fig. 2 as measured at 2 T, and discussed in detail below.

While the theoretical model does have some error with regard to the absolute intensity of the absorbance and MVCD bands, normalizing them in terms of the ratio of first moment of the MVCD and zeroth moment of the absorption, $\langle \Delta A \rangle_1 / \langle A \rangle_0$, which is directly related to the A_1 / D_0 ratio used to characterize MCD A-terms,42 largely corrects for errors in the electric dipole moment. A simple relationship between Zeeman g_J and MVCD A_1/D_0 values is obtained when there is no difference in g_J -values for the ro-vibrational ground and excited states.^{9–11} The g_J -values for the ${}^2\Pi_{1/2}$ have relatively weak dependence on J except for the first few low J's (eqn (9)). The ${}^{2}\Pi_{3/2}$ g_J values do change considerably with J but are predicted to become relatively constant at high J. These predicted g-value variations are summarized graphically in Fig. 6, and the parameter set used for calculation and tabulated g-values are provided in Tables S1 and S2 (ESI⁺).



Fig. 6 Graphical representation of the variation in *g*-values for the ${}^{2}\Pi_{3/2}$ (dash line) and ${}^{2}\Pi_{3/2}$ (solid line) $\nu = 0$ states using eqn (9) (tabulated values are in Table S2, ESI†). At this scale, *g*-values for $\nu = 1$ would be indistinguishable.

Since the transitions are resolved, straightforward moment analyses can be done for the ${}^{2}\Pi_{1/2}$ ro-vibrational transitions, at least for high *J*, to obtain their *g_J*-values.

We have done moment analysis of the spectra obtained at 0.2 and 2 Tesla, where the linear response is evident. The results for those ${}^{2}\Pi_{1/2}$ transitions (high *J*'s) that are rotationally resolved under our conditions are listed in Table 1 for the 2 T analysis and the 0.2 T values are available for comparison in Table S3 (ESI†). Our experimental determination of the g_{J} -values at 0.2 and 2 Tesla give averages of $\sim 2.4(3) \times 10^{-2}$ and $2.5(3) \times 10^{-2}$, respectively, for the resolved ${}^{2}\Pi_{1/2}$ transitions in both *P*- and *R*-branches These average *g*-values agree well with the theoretical ones for the ${}^{2}\Pi_{1/2}$ component (eqn (9),

Table 1 Experimental moment analysis results for the NO ${}^{2}\Pi_{1/2}$ transitions at 2 Tesla

	·	(() (10-5)	(4.4) (10-8)	$\langle \Delta A \rangle_1 / \langle A \rangle_0$	(10-2)
	ν_0/cm^{-1}	$\langle A \rangle_0 (10^{-5})$	$\langle \Delta A \rangle_1 (10^{\circ})$	(10^{-2})	$g_J (10^{-2})$
<i>R</i> (10.5)	1912.2	6.26	30.0	4.79	2.57
<i>R</i> (11.5)	1915.1	5.95	27.9	4.69	2.50
<i>R</i> (12.5)	1918.0	4.95	21.2	4.28	2.30
<i>R</i> (13.5)	1920.8	4.49	22.6	5.03	2.73
<i>R</i> (14.5)	1923.5	4.84	20.4	4.21	2.26
R(15.5)	1926.3	4.08	17.7	4.34	2.33
<i>R</i> (16.5)	1929.0	3.69	15.6	4.23	2.25
R(17.5)	1931.7	3.28	13.5	4.12	2.21
<i>R</i> (18.5)	1934.4	2.96	11.7	3.95	2.12
<i>R</i> (19.5)	1937.0	2.42	9.55	3.95	2.11
R(20.5)	1939.6	2.26	8.92	3.95	2.11
R(21.5)	1942.2			_	—
R(22.5)	1944.7	1.52	6.77	4.45	2.39
R(23.5)	1947.2	1.20	4.56	3.80	2.04
R(24.5)	1949.6		3.67	_	—
R(25.5)	1952.0	0.80	2.62	3.28	1.77
R(26.5)	1954.4	0.48	1.79	3.73	2.00
P(10.5)	1839.3	6.03	34.3	5.69	3.05
P(11.5)	1835.5	6.23	33.9	5.44	2.92
P(12.5)	1831.8	5.79	33.6	5.80	3.11
P(13.5)	1828.0	5.10	26.5	5.20	2.78
<i>P</i> (14.5)	1824.2	4.25	23.0	5.41	2.90
P(15.5)	1820.4	3.88	21.1	5.44	2.91
P(16.5)	1816.5	3.54	20.0	5.65	3.03
P(17.5)	1812.6	3.16	17.7	5.60	3.00
P(18.5)	1808.7	2.77	13.5	4.87	2.61
P(19.5)	1804.7	2.30	12.6	5.48	2.93
P(20.5)	1800.7	2.33	11.7	5.02	2.69
<i>P</i> (21.5)	1796.6	2.15	9.08	4.22	2.26

which average 2.6×10^{-2} for J = 2.5 to 25.5, see Table S2, ESI†). To our knowledge, this agreement provides a unique quantitative verification for Radford's theory for the ${}^{2}\Pi_{1/2}$ component based on a relatively large number of high *J*-states.

On the other hand, the theoretical g-values for the ${}^{2}\Pi_{3/2}$ component decrease from 0.778 for J = 1.5 to $\sim 2.6 \times 10^{-3}$ for J = 9.5, switch sign at J = 10.5 and then increase in magnitude with increasing J, becoming relatively stable at g about -0.019 by J = 22.5 (see Table S2, ESI†). Because of such a large change in the g_J -values, extraction of the g_J -values from just moment analysis of our MVCD and absorption data would be less well-grounded, although at high J values the predicted g_J is almost constant and the transitions are resolved. However, using an alternative approach, we can still verify Radford's theory for the ${}^{2}\Pi_{3/2}$ component in NO by comparing the experimental MVCD and absorption spectra with that simulated using the theoretical model.

A potential complication is that the simulated and experimental spectra have different contour shapes (J dependence of the intensity) for the P- and R-branches in both absorption and MVCD. This sort of disagreement was also observed for the diamagnetic molecules we studied and relates to the evaluation of the electric dipole transition moment and state population.^{9-11,46} Fortunately, this factor can be normalized out. The Zeeman g-value information is obtained by normalizing the MVCD, ΔA , to absorption, A (more strictly, ratioing the moments: $\langle \Delta A \rangle_1 / \langle A \rangle_0$). Therefore, the magnetic property which we desire to determine from our experiment, which depends on A_1/D_0 , will not change if the absorption and MVCD intensity variations are only due to the electric dipole moment and have same basic line shape, whose impact should be consistent for both.^{42,45} In other words, g_J determination is nearly independent of the electric dipole properties. Selected high J-value R- and P-branch transitions comparing the simulated and experimental spectra at 2 Tesla are shown in Fig. 7a and b, respectively.

Clearly we obtain excellent detailed agreement between simulations and experiment in this part of the spectral region in terms of shapes and relative intensities. The two transitions, ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$, are well resolved, and only the intensities of the two transitions differ with respect to each other, the ${}^{2}\Pi_{1/2}$ being computed to be too weak. This qualitative resemblance can be further tested in a quantitative manner by doing moment analysis on both the experimental and theoretical spectra, and by using the $\langle \Delta A \rangle_1 / \langle A \rangle_0$ normalization to obtain a measure of the degree of agreement between them. The A_1/D_0 and g_J-values were calculated using moment analysis of the simulated shapes and are listed in Table 2 for selected higher J-value transitions (${}^{2}\Pi_{1/2}$ component only), including those appearing in Fig. 7. The simulated A_1/D_0 and g-values (Table 2) can be directly compared to the experimental values presented in Table 1. The actual A and ΔA values differ between the tables, since the experimental absorbance is effectively arbitrary, being a function of pressure and path length. Hence, the simulations are scaled to give only order of magnitude agreement.

The same approach can be taken for selected resolved NO ${}^{2}\Pi_{3/2}$ component transitions, which are compared in Table 3 for simulated and experimental moment analyses. The A_{1}/D_{0} values



Fig. 7 NO *R*-branch experimental and simulated absorbance and MVCD for the R(16.5) to R(20.5) bands (left); and *P*-branch experimental and simulated absorbance and MVCD for the P(12.5) to P(15.5) bands (right), for the field of 2 T.

Table 2 Simulated moment analysis results for selected NO $^2\Pi_{1/2}$ transitions at 2 Tesla

	$ u_0/\mathrm{cm}^{-1} $	$\langle A angle_0 \ (10^{-4})$	$\langle \Delta A angle_1 \ (10^{-6})$	$\langle \Delta A angle_1 / \langle A angle_0$ (10 ⁻²)	$g_J (10^{-2})$
P(15.5)	1820.3	2.6026	12.513	4.808	2.575
P(14.5)	1824.2	3.1274	15.284	4.887	2.617
P(13.5)	1828.0	3.6796	18.258	4.962	2.657
P(12.5)	1831.8	4.2372	21.333	5.035	2.696
P(11.5)	1835.5	4.7694	24.331	5.101	2.732
<i>R</i> (16.5)	1929.1	2.2511	9.1049	4.045	2.166
R(17.5)	1931.9	1.7934	7.0737	3.944	2.112
<i>R</i> (18.5)	1934.5	1.4016	5.3906	3.846	2.060
<i>R</i> (19.5)	1937.2	1.0750	4.0280	3.747	2.007
<i>R</i> (20.5)	1939.8	0.8092	2.9538	3.650	1.955

Table 3 Moment analysis results for selected NO ${}^{2}\Pi_{3/2}$ transitions comparing simulated and experimentally measured (second line) A_{1}/D_{0} values at 2 T

	$ u_0/\mathrm{cm}^{-1}$	$\langle A \rangle_0$ (10 ⁻⁴)	$\langle \Delta A \rangle_1$ (10 ⁻⁶)	$\langle \Delta A angle_1 / \langle A angle_0$ (10 ⁻²)	A_1/D_0 (10 ⁻²)
P(15.5)	1818.6	1.37	-6.57	-4.80	-5.14
		0.36	-1.65	-4.58	-5.23
P(14.5)	1822.5	1.65	-8.06	-4.87	-5.13
		0.36	-1.76	-4.85	-5.19
P(13.5)	1826.6	1.96	-9.66	-4.94	-5.29
, í		0.44	-2.11	-4.78	-5.12
P(12.5)	1830.3	2.26	-11.31	-5.00	-5.36
. ,		0.45	-2.15	-4.78	-5.09
R(16.5)	1930.2	1.18	-4.76	-4.04	-4.33
		0.27	-1.11	-4.11	-4.49
R(17.5)	1932.9	0.93	-3.68	-3.94	-4.22
		0.24	-0.96	-4.02	-4.44
R(18.5)	1935.6	0.72	-2.78	-3.84	-4.12
		0.22	-0.82	-3.66	-4.04
R(19.5)	1938.3	0.55	-2.06	-3.74	-4.01
. /		0.19	-0.69	-3.60	-3.97
R(20.5)	1941.0	0.41	-1.50	-3.65	-3.91
. ,		0.16	-0.55	-3.54	-3.90

obtained from both spectra are close in value, even though the actual intensities differ, which confirm that our experimental results quantitatively support Radford's prediction for the NO ${}^{2}\Pi_{3/2}$ component in terms of magnetic properties. While we do not provide g_{J} values because they vary with J for the 3/2 state, the value would be roughly half the A_{1}/D_{0} values.

However, there is significant difference in the simulated and experimental spectra, at least for some medium *Js*, for example, compare Fig. 2 and 5, especially R(1.5)-R(6.5). We even observed strong dependence of the absorption intensity on the field strength for some medium *J* values, ${}^{2}\Pi_{3/2}$ transitions (for example, see Fig. 4), which is not predicted in the simulated spectra. This might be caused by the inadequacy of the adopted theory for the strong field measurement.

In principle, there should be a possibility of observing B and C-terms^{42,45,47,48} in such an MVCD experiment. B-terms, representing the contribution to MVCD from field-induced interaction between molecular eigenstates, give rise to absorption-like MVCD bands. C-terms arise from transitions involving a degenerate ground state due to the unequal population of the magnetic components of the initial state. They also lead to absorption-like MVCD bands and can only be identified by analysis of the temperature variation of MVCD spectra. This can be made more complex by any phase errors in the FTIR measurement, since determination of the precise value of the zero-path-difference (ZPD) of the interferogram can affect the MVCD band shape. In our experiments, the ZPD was determined as the point of symmetry in the interferogram using a second detector technique and was confirmed by comparing to results of CO MVCD spectra (which has no C-term possibility) measured under identical conditions as NO.³⁸ For the NO MVCD, all the peaks, when properly phase corrected, are dominated by an apparent A-term character, and therefore, the B-term and C-term contributions to the MVCD, if they exist, must be much weaker.

Conclusions

The MVCD spectra for the NO molecule fundamental, in terms of the $\Delta A/A$ ratio, have 3 orders of magnitude stronger intensity than found for diamagnetic molecules due to the unpaired electron in NO. The MVCD observed for the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ transitions at all five fields studied showed easily measured spectra over the entire band, including all *J*-values. This ensemble of data provides a more complete data set than previously available for demonstration that NO has considerable deviation from Hund's coupling case (a). The good agreement between the simulations based on Radford's theory

Downloaded by Ustav Organicke AV on 26 July 2012 Published on 26 April 2012 on http://pubs.rsc.org | doi:10.1039/C2CP40950J and our experimental data, in terms of the derived magnetic properties, offers an experimental verification of the theory for a relatively large number of *J*-value transitions. The MVCD A_1/D_0 ratio is given by fundamental physical constants, determined directly from the moment analysis of measured spectra from $\langle \Delta A \rangle_1 / \langle \Delta A \rangle_0$ and does not contain molecular properties other than terms associated with the energy. The MVCD method provides a direct path to the sign and magnitude of the g_J values which can be used to analyze the spin–orbital-rotational angular momentum coupling in such gas phase radicals. These MVCD measurements can be done with medium resolution FTIR spectrometers using modest magnetic fields, providing access to high resolution data for relatively small effort. Finally, this molecule provides the strongest magnetic circular dichroic signal measured so far.

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