Terahertz spectroscopy of $^{18}$O and isotopic invariant fit of several nitric oxide isotopologs

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Abstract

A tunable far-infrared laser sideband spectrometer was used to investigate a nitric oxide sample enriched in $^{18}$O between 0.99 and 4.75 THz. Regular, electric dipole transitions were recorded between 0.99 and 2.52 THz, while magnetic dipole transitions between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin-ladders were recorded between 3.71 and 4.75 THz. These data were combined with lower frequency data of $^{18}$O (unlabeled atoms refer to $^{14}$N and $^{16}$O, respectively), with rotational data of NO, $^{15}$NO, $^{17}$O, and $^{15}$N$^{18}$O, and with heterodyne infrared data of NO to be subjected to one isotopic invariant fit. Rotational, fine and hyperfine structure parameters were determined along with vibrational, rotational, and Born-Oppenheimer breakdown corrections. The resulting spectroscopic parameters permit prediction of rotational spectra suitable for the identification of various nitric oxide isotopologs especially in the interstellar medium by means of rotational spectroscopy.

Keywords: nitric oxide, terahertz spectroscopy, electric dipole transitions, magnetic dipole transitions, fine structure, hyperfine structure

1. Introduction

Nitric oxide, NO, is the only stable diatomic molecule with an odd number of electrons. It is, therefore, of great interest for fundamental sciences and in particular for molecular spectroscopy. This is an important reason for a large body of spectroscopic investigations into the ground $^2\Pi$, electronic state of NO. Soon after an electron paramagnetic resonance study of NO in 1950 [1], the first reports on its rotational spectrum in the ground vibrational state appeared [2,3,4]. Further studies were carried out later on the main isotopolog [5,6,7,8,9], on $^{15}$NO [7,8,9], on $^{18}$O [7,8,9], and even on $^{15}$N$^{17}$O and $^{15}$N$^{18}$O [10]; unlabeled atoms refer to $^{14}$N and $^{16}$O. The $\Lambda$-doubling transitions in the radio-frequency (RF) and microwave (MW) regions were studied extensively for NO and $^{15}$NO in their ground vibrational states [11] with additional data for NO [12,13,14,15], even in its excited vibrational state $v = 1$ [14,15]. The spin-orbit splitting in $v = 0$ was determined directly from high-resolution observations of the $^2\Pi_{1/2} \leftrightarrow ^2\Pi_{3/2}$ magnetic dipole spectrum of NO [8,16] and of $^{15}$NO [8] near 123 cm$^{-1}$. Numerous infrared (IR) studies have been carried out, mostly on the main isotopic species. Among those with experimental transitions frequencies we mention in particular heterodyne [17] and Lamb-dip heterodyne studies [18] of the fundamental vibrational band, which was also recorded with Fourier transform spectroscopy (FTS) [19,20,21]. Much higher vibrational levels were accessed through emission spectroscopy of the first [22,23] and second overtone [24]. Isotopic data are also available, albeit to a lesser extent [25,26].

The spectroscopy of NO is also important for diagnostic purposes. Nitric oxide is a minor constituent of Earth’s atmosphere with a prominent role in the catalytic decomposition of ozone in the stratosphere. However, it is not easily detected in the atmosphere employing rotational spectroscopy because of its small dipole moment of 0.15872 (2) D [12], high-resolution IR spectroscopy of its fundamental band is commonly used instead. In fact, we are only aware of one report on microwave observations of atmospheric NO [27]. The NRAO 11 m telescope on Kitt Peak was used to to record the $J = 2.5/1 \leftrightarrow 1.5/1$ transition of NO near 250.8 GHz. Filtering out emission with line widths larger than 1.5 MHz, they were sensitive only to NO at high altitudes of $> 50$ km. Radio astronomy, on the other hand, was used frequently to observe NO in space. Nitric oxide was detected in the star-forming region Sagittarius B2(OH) [28] and in dark clouds [29]. Its abundance in these dense molecular clouds is rather high, around that of C$^{18}$O [30], so it was hardly surprising that it was also detected in external galaxies such as the star-burst galaxy NGC 253 [31]. Higher rotationally excited transitions of NO have been observed with the high-resolution instrument HIFI on board of the Herschel space observatory in the frame work of molecular line surveys of the prolific star-forming regions Orion KL [32] and Sagittarius B2(N) [33]. The Atacama Large Millimeter Array (ALMA), which is currently under construction, will provide not only very high spatial resolution, but also very high sensitivity and spectral resolution, which should facilitate the detection of minor isotopic species of NO.

We recorded magnetic dipole transitions of $^{18}$O around 4 THz to determine the spin-orbit splitting directly. In addition,
we recorded electric dipole transitions around 2 THz for better prediction of higher rotational states. The resulting data were combined with other $^{18}$O rotational data to determine its spectroscopic parameters. Ultimately, the data were also combined with rotational data of other NO isotopologs and with heterodyne IR data of the main species for an isotopic invariant fit along with Born-Oppenheimer breakdown (BOB) corrections to derive, in turn, predictions of the rotational spectra of NO isotopic species for radio astronomy.

2. Experimental details and observed spectrum

The terahertz spectrometer used at the University of Toyama in the present study is a so-called Evenson-type tunable far-infrared spectrometer (TuFIR) based on a frequency synthesizing technique developed by Evenson and co-workers [34]. Details of the spectrometer can be found elsewhere [35]. The basic principle is the stable far-infrared generation by the difference frequency generated from two frequency-stabilized CO$_2$ lasers. The difference frequency is mixed with the microwave radiation from a synthesized sweeper on a metal-insulator-metal (MIM) diode to achieve tunability. Two side bands (upper and lower) are generated. The frequency of the absorption can be determined by the phase of the signal. A liquid-helium-cooled Si bolometer is used to detect the terahertz radiation. The 1/f detection signal from the lock-in amplifier was recorded with a computer. A path length modulator was inserted into the terahertz path in order to eliminate standing waves.

Two glass cells, 250 cm or 40 cm long, were used for most of the measurements. The isotopically enriched N$^{18}$O (Shoko Co. Ltd., 97% $^{18}$O) was used without further purification. The sample pressure was maintained at about 7 - 12 Pa for the pure rotational (electronic dipole) transitions and at ~120 Pa for the weak magnetic transitions. All measurements were carried out at room temperature.

![Figure 1: Terahertz spectrum of N$^{18}$O in the region of the $^{2}\Pi_{3/2} \leftarrow ^{2}\Pi_{1/2}$, $Q(9.5')$ fine structure transition with resolved $^{14}$N hyperfine splitting.](image)

**Table 1:** Rotational (electric dipole) transitions of N$^{18}$O, frequency (MHz) and residuals O−C (MHz) between observed frequency and that calculated from the isotopic invariant fit.

| $\Omega$ | $^{2}\Pi_{1/2}$ | Frequency | O−C |
|---------|-----------------|-----------|------|
| $^{2}\Pi_{1/2}$ | 10.5$^a$ − 9.5$^a$ | 998325.402 | 0.037 |
| $^{2}\Pi_{1/2}$ | 10.5$^a$ − 9.5$^a$ | 998824.023 | 0.061 |
| $^{2}\Pi_{1/2}$ | 10.5$^a$ − 9.5$^a$ | 1024876.524 | −0.074 |
| $^{2}\Pi_{1/2}$ | 11.5$^a$ − 10.5$^a$ | 1093603.395 | 0.012 |
| $^{2}\Pi_{1/2}$ | 11.5$^a$ − 10.5$^a$ | 1093894.752 | 0.061 |
| $^{2}\Pi_{1/2}$ | 11.5$^a$ − 10.5$^a$ | 1122177.958 | 0.027 |
| $^{2}\Pi_{1/2}$ | 11.5$^a$ − 10.5$^a$ | 1122224.596 | 0.065 |
| $^{2}\Pi_{1/2}$ | 12.5$^a$ − 11.5$^a$ | 1188668.423 | 0.017 |
| $^{2}\Pi_{1/2}$ | 12.5$^a$ − 11.5$^a$ | 1188952.059 | 0.026 |
| $^{2}\Pi_{1/2}$ | 12.5$^a$ − 11.5$^a$ | 1219450.321 | 0.074 |
| $^{2}\Pi_{1/2}$ | 12.5$^a$ − 11.5$^a$ | 1219504.465 | 0.012 |
| $^{2}\Pi_{1/2}$ | 13.5$^a$ − 12.5$^a$ | 1283718.135 | 0.012 |
| $^{2}\Pi_{1/2}$ | 13.5$^a$ − 12.5$^a$ | 1283993.739 | 0.024 |
| $^{2}\Pi_{1/2}$ | 13.5$^a$ − 12.5$^a$ | 1316649.397 | 0.027 |
| $^{2}\Pi_{1/2}$ | 13.5$^a$ − 12.5$^a$ | 1316711.601 | 0.044 |
| $^{2}\Pi_{1/2}$ | 14.5$^a$ − 13.5$^a$ | 1378750.049 | 0.040 |
| $^{2}\Pi_{1/2}$ | 14.5$^a$ − 13.5$^a$ | 1379017.279 | 0.026 |
| $^{2}\Pi_{1/2}$ | 14.5$^a$ − 13.5$^a$ | 1413770.721 | −0.029 |
| $^{2}\Pi_{1/2}$ | 14.5$^a$ − 13.5$^a$ | 1413841.225 | −0.019 |
| $^{2}\Pi_{1/2}$ | 15.5$^a$ − 14.5$^a$ | 1473761.367 | 0.031 |
| $^{2}\Pi_{1/2}$ | 15.5$^a$ − 14.5$^a$ | 1474020.025 | 0.065 |
| $^{2}\Pi_{1/2}$ | 15.5$^a$ − 14.5$^a$ | 1510810.030 | −0.008 |
| $^{2}\Pi_{1/2}$ | 15.5$^a$ − 14.5$^a$ | 1510889.084 | −0.039 |
| $^{2}\Pi_{1/2}$ | 16.5$^a$ − 15.5$^a$ | 1568749.227 | 0.051 |
| $^{2}\Pi_{1/2}$ | 16.5$^a$ − 15.5$^a$ | 1568998.950 | 0.001 |
| $^{2}\Pi_{1/2}$ | 19.5$^a$ − 18.5$^a$ | 1835339.862 | 0.038 |
| $^{2}\Pi_{1/2}$ | 19.5$^a$ − 18.5$^a$ | 1835761.992 | −0.033 |
| $^{2}\Pi_{1/2}$ | 19.5$^a$ − 18.5$^a$ | 1898181.516 | 0.036 |
| $^{2}\Pi_{1/2}$ | 26.5$^a$ − 25.5$^a$ | 2516576.862 | −0.065 |
| $^{2}\Pi_{1/2}$ | 26.5$^a$ − 25.5$^a$ | 2516732.584 | −0.046 |

*a* Uncertainty 50 kHz for each rotational line.
The N^{18}O rotational transitions were found easily based on predictions generated from previous work \[8, 9\]. Hyperfine structure (HFS) was not resolved in these transitions, and good signal-to-noise ratios (SNR) were obtained. Uncertainties of 50 kHz were assigned to these data which are gathered in Table 1. Combining our new data with the previous ones and taking into account the fine structure (FS) splitting in NO and \(^{18}\)NO \[8\], the weaker magnetic dipole transition were observed readily. As can be seen in Fig. 1, HFS was resolved in these spectral recordings, and the SNR were reasonable. We assigned uniformly 250 kHz as uncertainties to these transition frequencies mainly because of the lower SNR, but also because of the larger line width caused by pressure broadening. The magnetic dipole transitions are summarized in Table 2.

### Table 2: \(^{2}\)Π\(_{1/2} \rightarrow \(^{2}\)Π\(_{1/2}\) magnetic dipole (fine structure) transitions of N\(^{18}\)O.

| Frequency (MHz) | O–C (MHz) |
|-----------------|-----------|
| 9.5' – 9.5' | 10.5 – 10.5 | 3719850.891 | 0.025 |
| 9.5' – 9.5' | 9.5 – 9.5 | 371990.708 | 0.097 |
| 9.5' – 9.5' | 8.5 – 8.5 | 3719968.880 | 0.152 |
| 9.5' – 9.5' | 8.5 – 8.5 | 3722980.772 | 0.047 |
| 9.5' – 9.5' | 9.5 – 9.5 | 372300.929 | 0.052 |
| 9.5' – 9.5' | 10.5 – 10.5 | 3723081.461 | 0.027 |
| 10.5' – 10.5' | 11.5 – 11.5 | 3745903.244 | 0.302 |
| 10.5' – 10.5' | 10.5 – 10.5 | 3745963.357 | 0.121 |
| 10.5' – 10.5' | 9.5 – 9.5 | 3746023.090 | 0.049 |
| 10.5' – 10.5' | 9.5 – 9.5 | 3749294.640 | 0.089 |
| 10.5' – 10.5' | 10.5 – 10.5 | 3749343.231 | 0.055 |
| 10.5' – 10.5' | 11.5 – 11.5 | 3749391.245 | 0.028 |
| 4.5' – 3.5' | 5.5 – 4.5 | 405364.418 | 0.057 |
| 4.5' – 3.5' | 4.5 – 3.5 | 405364.401 | 0.000 |
| 4.5' – 3.5' | 3.5 – 2.5 | 405378.502 | 0.054 |
| 4.5' – 3.5' | 3.5 – 2.5 | 405496.173 | 0.226 |
| 4.5' – 3.5' | 4.5 – 3.5 | 4055021.910 | 0.696 |
| 4.5' – 3.5' | 5.5 – 4.5 | 4055035.883 | 0.279 |
| 6.5' – 5.5' | 7.5 – 6.5 | 427456.109 | 0.446 |
| 6.5' – 5.5' | 6.5 – 5.5 | 427432.120 | 0.416 |
| 6.5' – 5.5' | 5.5 – 4.5 | 427437.189 | 0.056 |
| 6.5' – 5.5' | 5.5 – 4.5 | 427629.069 | 0.396 |
| 6.5' – 5.5' | 6.5 – 5.5 | 427631.183 | 0.024 |
| 6.5' – 5.5' | 7.5 – 6.5 | 427640.386 | 0.417 |
| 7.5' – 6.5' | 8.5 – 7.5 | 438826.502 | 0.117 |
| 7.5' – 6.5' | 7.5 – 6.5 | 438830.480 | 0.058 |
| 8.5' – 6.5' | 7.5 – 5.5 | 438838.531 | 0.081 |
| 7.5' – 6.5' | 5.5 – 4.5 | 439064.905 | 0.072 |
| 7.5' – 6.5' | 6.5 – 5.5 | 439069.621 | 0.274 |
| 7.5' – 6.5' | 7.5 – 6.5 | 439076.122 | 0.257 |
| 9.5' – 8.5' | 10.5 – 9.5 | 462346.645 | 0.168 |
| 9.5' – 8.5' | 9.5 – 8.5 | 462352.062 | 0.214 |
| 9.5' – 8.5' | 8.5 – 7.5 | 462389.493 | 0.149 |
| 9.5' – 8.5' | 8.5 – 7.5 | 462653.285 | 0.095 |
| 9.5' – 8.5' | 8.5 – 8.5 | 462658.085 | 0.253 |
| 9.5' – 8.5' | 10.5 – 9.5 | 462662.944 | 0.211 |
| 10.5' – 9.5' | 11.5 – 10.5 | 474451.295 | 0.439 |
| 10.5' – 9.5' | 10.5 – 9.5 | 474462.399 | 0.063 |
| 10.5' – 9.5' | 9.5 – 8.5 | 474468.692 | 0.032 |
| 10.5' – 9.5' | 9.5 – 8.5 | 474798.294 | 0.194 |
| 10.5' – 9.5' | 10.5 – 9.5 | 474802.065 | 0.254 |
| 10.5' – 9.5' | 11.5 – 10.5 | 474808.730 | 0.024 |

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\(a\) Uncertainty 250 kHz for each fine structure line.

### 3. Spectroscopic analysis

NO is a stable radical with a regular \(^2\)Π ground electronic state, i.e., the \(^2\)Π\(_{1/2}\) spin ladder is at lower energies than the \(^2\)Π\(_{1/2}\) spin ladder. It has a fairly small electric dipole moment of 0.15872 (2) D \[12\]. As a diatomic consisting of two fairly light atoms, its spin-orbit splitting is comparatively small (~3.7 THz) while its rotational constant is with ~51 GHz fairly large. As a consequence, its spectrum is close to Hund’s case (a) at lower rotational quantum numbers, but closer to Hund’s case (b) at intermediate and higher rotational quantum numbers.

The effective Hamiltonian suitable to fit the rotational spectrum of NO has been described rather often, and a rather detailed description can be found in Ref. \[8\]. Further discussion on the Hamiltonian of a \(^2\)Π molecule in terms of Hund’s cases (a) and (b) can be found elsewhere \[36\]. Pickett’s SPICE and SFINIT programs \[37\] were used for prediction and fitting of the NO spectra. The programs were intended to be rather general, thus being able to fit asymmetric top rotors with spin and vibration-rotation interaction in support of the spectral line lists of the Jet Propulsion Laboratory (JPL) \[38\] and Cologne Database for Molecular Spectroscopy (CDMS) \[39, 40\]. Hund’s case (b) quantum numbers are employed in SPICE and SFINIT whereas Hund’s case (a) quantum numbers are more common for NO. We follow the latter labeling in Fig. 1 and Tables 1 and 2. Conversion of Hund’s case (b) quanta to case (a) or vice versa depends on the magnitude of the rotational energy relative to the magnitude of the spin-orbit splitting. For \(2B(J)\approx0.5(J+0.5)\approx[A]\), levels with \(J+0.5=N\) correlate with \(^2\)Π\(_{1/2}\) and levels with \(J-0.5=N\) correlate with \(^2\)Π\(_{3/2}\); for larger values of \(J\), the correlation is reversed. In the case of the NO isotopologs, the reversal occurs between \(J=5.5\) and \(J=6.5\).

During the fitting process, we contained a spectroscopic parameter in the fit if it reduced the rms error of the fit, as measure of the quality of the fit, by an appreciable amount. This meant in most instances that the parameter was determined with great significance, meaning its uncertainty in the fit was about one fifth of the magnitude of its value or less. Care was also taken to evaluate which parameter reduced the rms error by the greatest amount.
Among the available data of one isotopic species and within one vibrational state, we used those, which were most accurate because data with larger uncertainties have considerably lower weights in the fit; the weight of a datum in the fit scales inversely to the square of the uncertainty. In a few cases, multiple data were used if the uncertainties were similar. We scrutinized the reported uncertainties in all instances. For the great majority of the data, the reported values were employed in the fit. Few transition frequencies were omitted from the fit if their residuals in the fits were much larger than the reported uncertainties. In few other cases with large residuals, the uncertainties were increased. Some uncertainties appeared to be conservative, and they were reduced somewhat. Details will be given below.

In order to evaluate \( ^{18}\text{N}\text{O} \) spectroscopic parameters, we combined our data with the lower frequency data from Saleck et al. [7]. Uncertainties assigned to the transition frequencies pertaining to the lowest quantum numbers of the \( ^2\Pi_{1/2} \) ladder (\( J = 1.5-0.5 \) and 2.5–1.5) appeared to be too conservative, not only for \( ^{18}\text{O} \) [7] in the single isotopolog fit, but also in the combined fit and for \( ^{15}\text{N}\text{O} \) [7], and for \( ^{17}\text{N}\text{O} \) and \( ^{15}\text{N}^{18}\text{O} \) [10]; therefore, we reduced the uncertainties somewhat for these transitions. We omitted the data from Ref. [9] because they had slightly to considerably larger uncertainties, and the data with only slightly larger uncertainties had residuals frequently much larger than the quoted uncertainties.

The initial spectroscopic parameter set consisted of those employed for NO and \( ^{15}\text{NO} \) [8]. It is worthwhile mentioning that \( \gamma \) was used there and in the present fits whereas most other NO parameter sets employed \( \gamma_B \) instead. \( \gamma_B \) and \( \gamma_C \) make essentially indistinguishable contributions in a \( ^2\Pi \) radical, and the same holds for their vibrational or rotational corrections [41]; only one of the two parameters can be determined usually. One way to resolve the indeterminacy is an isotopic invariant fit [22], which will be described for NO in the following part of this section. If at least one of the atoms of the molecule has a non-zero spin, the combination of HFS and Zeeman effects may allow to disentangle \( \gamma_B \) and \( \gamma_C \); it turned out that in NO the contributions come almost entirely from \( \gamma \), whereas \( \gamma_B \) dominated the contributions in FO [43]. Several of the initial parameters in the \( ^{18}\text{O} \) fit were poorly determined and were omitted successively from the fit without increasing the rms error much. The nuclear spin-rotation parameter \( C_{ij} \) was retained in the fit despite being not determined significantly because its omission increased the rms error by more than 5% and because its value was correct within its uncertainty. The final set of \( ^{18}\text{O} \) spectroscopic parameters is given in Table 3.

The ro-vibrational energy levels of a diatomic molecule AB, such as NO, can be represented by the Dunham expression [44]

\[
E(\nu, J)/\hbar = \sum_{ij} Y_{ij}(\nu + 1/2)^i(N(N + 1))^j, \tag{1}
\]

where the \( Y_{ij} \) are the Dunham parameters. In electronic states different from \( \Sigma \) states, i.e., in states with orbital angular momentum \( \Lambda > 0 \), the expansion in \( N(N + 1) \) is often replaced by an expansion in \( N(N + 1) - \Lambda^2 \), see, e.g., Ref. [45]. The ground electronic state of NO is \( ^2\Pi (\Lambda = 1) \), and the expansion is often carried out in \( N(N + 1) - 1 \), and this expansion was used here. The expansion in \( N(N + 1) \) is quite common also, see, e.g., the case of the \( ^3\Sigma \) radical \( \text{BrO} \) [46].

Several isotopic species of AB can be fit jointly by constraining the \( Y_{ij} \) to [35, 47]

\[
Y_{ij} = U_{ij} \left( 1 + \frac{m_e A_{ij}^A}{M_A} + \frac{m_e A_{ij}^B}{M_B} \right) \mu^{-i(\nu + 2)/2} \tag{2}
\]

where \( U_{ij} \) is isotopic invariant, \( m_e \) is the mass of the electron, \( \mu \) is the reduced mass of AB, \( M_A \) is the mass of atom A, and \( A_{ij}^A \) is a BOB term associated with atom A. The abbreviation \( \delta_{ij} \) is sometimes used for \( U_{ij} \mu^{-i(\nu + 2)/2} A_{ij}^A m_e / M_A \). We need to point out that both \( A_{ij}^A \) and \( \delta_{ij} \) are defined negatively in some publications. Obviously, \( A_{ij}^A \) and \( \delta_{ij} \) are defined equivalently.

Rotational and vibrational corrections to the \( \Lambda \)-doubling, FS, and HFS parameters have been expressed analogously as in Eqs. (1) and (2), the isotopic dependences were given explicitly, e.g., in Refs. [36, 46]. Briefly, the lowest order fine structure parameters \( A_{00} \) and \( \gamma_{00} \) scale with 1 and \( \mu^{-1} \), respectively. The \( \Lambda \)-doubling parameters \( p_{00} \) and \( q_{00} \) scale with \( \mu^{-1} \) and \( \mu^{-2} \), respectively. The electron spin-nuclear spin coupling parameters \( a_{00} \), \( b_{F,00} \), \( c_{00} \), and \( d_{00} \) all scale with the respective nuclear \( g \) factor \( g_N \). In the case of nitrogen, both \( ^{14}\text{N} \) and \( ^{15}\text{N} \) have non-zero spins (\( I = 1 \) and 0.5, respectively). The \( ^{15}\text{N}^{16}\text{N} \) \( g \) factor ratio is \(-1.4027548 \) [48, 29]. There is only one oxygen nucleus, \( ^{16}\text{O} \), with non-zero spin of \( 5/2 \), so no \( g \) factor ratios needed to be considered for oxygen substitution. The lowest order quadrupole parameters, \( eQ_{Q,00} \), \( eQ_{Q^2,00} \), and \( eQ_{Q^3,00} \) all scale with the quadrupole moment \( Q \), but there is only one nucleus for each atom with \( I \geq 1 \), \( ^{14}\text{N} \) and \( ^{16}\text{O} \). The lowest order nuclear spin-rotation parameters \( C_{I,00} \) and \( C'_{I,00} \) scale with \( g_N \).
Isotopic invariant fits were carried out for numerous diatomics, among them BrO [46], CdH [50, 51], ZnH [51], CH⁺ [52], and O₂ [53]. The atomic masses were taken from a recent compilation [55]. It includes recent improvements for ¹⁴N [50], ¹⁸O [57], and ¹⁷O [59]. Among these, the updated ¹⁸O value is the most relevant one for high resolution spectroscopy.

The aim of the present study was modeling of the ground state rotational spectra of NO isotopic species. However, in order to separate contributions of the breakdown of the Born-Oppenheimer approximation to a certain spectroscopic parameter from the frequently larger vibrational correction to this parameter, see e.g., Refs. [50, 51], we needed to consider some information on vibrationally excited NO. These were NO v = 1 Δ-doubling data [14, 15] along with heterodyne v = 1–0 IR transition frequencies [17, 18]. A subsequent study will consider the extensive available IR data. The study should include not only experimental transition frequencies with appropriate uncertainties, but also intensity information from experimental measurements as well as from empirical and theoretical modeling [59].

We started the combined analysis by determining spectroscopic parameters for the ground vibrational state of the main isotopolog. As in Ref. [5], electric and magnetic dipole transitions in the THz region were taken from that work, and RF and MW Δ-doubling data were taken from Refs. [11, 12, 13, 14, 15]. We used also unpublished data from Pickett et al. [5] which had been used in prior analyses [6, 7, 13]. These data were not only of similar accuracy as the THz data [8], but also extended from the lowest J = 1.5–0.5 up to J = 4.5–3.5. In contrast, the THz data started at J = 3.5–2.5 and J = 4.5–3.5 for the ²Π₁/₂ and ³Π₃/₂ spin components, respectively [5]. One transition frequency from Ref. [5], (350989.583 ± 0.020) kHz, was omitted from the fit because the residual was about five times the uncertainty. The three transition frequencies from Ref. [13] with reported uncertainties of 1, 1, and 2 kHz, respectively, were assigned uncertainties of 3 kHz in accordance with the residuals. Ground and excited state Δ-doubling data from Ref. [14] appeared to be judged too conservatively with uncertainties of 20 or 25 kHz. They were reproduced to within 5 kHz for the most part even with the reported uncertainties. Thus we used 5 kHz as uncertainty for each of these lines. Approximately 30 kHz were reported as uncertainties for the ground and excited state Δ-doubling data from Ref. [15]. We assigned 20 kHz to all of the v = 1 data and to most of the v = 0 data; 50 kHz were attributed to the J = 20.5–20.5 data which appeared to require a larger uncertainty of 30 or 50 kHz.

The choice of spectroscopic parameters for NO in its ground vibrational state was straightforward for the most part based on previous analyses [8, 13]. The distortion parameter dₛ₆ ≈ 4₀₂ had uncertainties in the fits slightly smaller than in Ref. [8], but its value was much smaller in magnitude and not determined with significance; the value obtained with the final line list was (−2.9 ± 2.0) × 10⁻¹⁰ MHz. Hence, it was omitted from the final fit, as was done in Ref. [18]. No distortion correction was needed for any of the HFS parameters with the exception of d. It was necessary to include eQₓₜₑ(N) in the fit to reproduce the A-doublet data from Ref. [11] well. This parameter describes the difference in eQₓ within the ²Π₁/₂ and ³Π₃/₂ spin components. It was used, e.g., in a previous study of BrO [46]. The approach in the original A-doublet study [11] was equivalent, because two independent parameters ε₁ and ε₂ were used to determine the ¹⁴N quadrupole coupling within the ²Π₁/₂ and ³Π₃/₂ substates, respectively.

Vibrational corrections were evaluated next by including heterodyne IR measurements of the NO v = 1–0 fundamental band [17, 18] with reported uncertainties in the fit and subsequently the A-doublet transition frequencies of NO in its excited vibrational state [13, 15] with uncertainties as described above. The choice of parameters to be included in the fit was straightforward for the most part. After inclusion of dₛ₆ in the fit at most two of the three vibrational corrections to a, bₓ, and c could be determined. The best result was obtained in the final fits with vibrational corrections to a and bₓ. Each of these parameters led to a modest reduction of the rms error. In case of the ¹⁴N quadrupole parameters, a vibrational correction was only needed for eQₓₜₑ(N).

Inclusion of the ¹⁵NO A-doublet transitions [11] into the fit turned out to be challenging. In fact, whereas the ³Π₃/₂ data were fit very satisfactorily in the original study [11], none of the ²Π₁/₂ transition frequencies was reproduced there within the uncertainties. They showed deviations between more than 5 times to almost 70 times the quoted uncertainties [11]. Interestingly, our initial trial fits of the ¹⁵NO data lead only to a rejection of the ΔF ≠ 0, J = 1.5 transition of the ²Π₁/₂ ladder at (84.589 ± 0.002) MHz because of a residual of 13 kHz. In the combined fit, two ²Π₁/₂ A-doublet transition frequencies with J = 0.5 and ΔF ≠ 0 were omitted in addition because each one deviated from the calculated frequency by about 40 times the reported uncertainty; furthermore, two corresponding frequencies with J = 1.5 deviated each by about 8 times the reported uncertainty and were omitted also. All other transitions were retained in the fit with the uncertainties as reported. The rotational [7, 8] and FS transition frequencies [8] were included with the reported uncertainties, except for the modifications in the low-J data [7] as mentioned above.

The inclusion of the ¹⁵NO data called for BOB parameters for Y₀₁ and A₀₀ to be included in the fit, as was expected. In addition, BOB parameters were required for Y₀₂ and p₀₀ because transition frequencies with very high rotational quantum numbers were determined for NO and for ¹⁵NO [8].

Subsequently, N¹⁷O data were used in the fit as described above. Only BOB parameters for Y₀₁ and A₀₀ were needed because the N¹⁰O data did not reach as high quantum numbers as the NO and ¹⁵NO data. Inclusion of ¹⁵N¹⁰O data did not afford any additional parameters. Finally, the N¹⁷O data were used in the fit. Obviously, new parameters were necessary to account for the ¹⁷O HFS splitting; no other parameters were introduced to the fit. The final set of spectroscopic parameters determined in the fit is given in Table 4; derived parameters are presented in Table 5.

All input data were reproduced on average to within the uncertainties employed in the fit; the rms error of the fit is 0.924. There is some scatter among the various subdata sets, but none
Table 4: Spectroscopic parameters\(^a\) (MHz) for NO determined from the isotopic invariant fit.

| Parameter                  | Value               |
|----------------------------|---------------------|
| \(\gamma_{10}^{\text{iso}}\) \(\times 10^3\) | 56.240.216.66 (14) |
| \(U_{10}\)                  | 51.119.680.7 (42)  |
| \(U_{10}^{\text{iso}}\) \(\times 10^3\) | \(-4.469.2 (29)\)  |
| \(U_{10}^{\text{iso}}\) \(\times 10^3\) | \(-4.027.2 (27)\)  |
| \(Y_{11}\)                  | \(-526.763 (32)\)  |
| \(U_{22}^{\text{iso}}\) \(\times 10^3\) | \(-16.3.944 (30)\) |
| \(U_{22}^{\text{iso}}\) \(\times 10^3\) | \(-16.3.944 (30)\) |
| \(Y_{12}\)                  | \(-0.484 (25)\)    |
| \(Y_{03}\)                  | \(-37.940 (114)\)  |
| \(A_{10}\)                  | \(-7.335.247 (59)\) |
| \(\gamma_{01}\)            | \(-0.123 (89)\)    |
| \(\gamma_{10}\)            | \(-193.40 (21)\)   |
| \(\gamma_{10}\)            | \(-7.476 (55)\)    |
| \(\gamma_{01} \times 10^3\) | \(-1.611 (56)\)    |
| \(\sigma_{BO}^{\text{NO}}\) | \(-3.523.4 (99)\)  |
| \(\sigma_{BO}^{\text{NO}}\) | \(-17.11 (93)\)    |
| \(\sigma_{NO}^{\text{NO}}\) | \(-403.50 (32)\)   |
| \(\sigma_{NO}^{\text{NO}}\) | \(-3.1 (12)\)      |
| \(q_{10}\)                  | \(-2.94.71 (30)\)  |
| \(q_{10} \times 10^3\)     | \(-4.42.65 (26)\)  |
| \(q_{10} \times 10^6\)     | \(-4.23.19 (126)\) |
| \(\delta_{NO}(N)\)         | \(-8.34.02 (106)\) |
| \(\delta_{NO}(N) \times 10^3\) | \(-2.02.3 (211)\) |
| \(\delta_{NO}(N) \times 10^6\) | \(-2.23.71 (21)\) |
| \(\delta_{NO}(N) \times 10^9\) | \(-2.49 (43)\)    |
| \(\delta_{NO}(N) \times 10^9\) | \(-5.89.80 (41)\) |
| \(\delta_{NO}(N) \times 10^9\) | \(-1.12.69 (14)\) |
| \(\epsilon\) \(\times 10^3\) | \(-3.03 (27)\)    |
| \(\epsilon\) \(\times 10^6\) | \(-1.06 (14)\)    |
| \(\epsilon\) \(\times 10^9\) | \(-1.89.86 (32)\) |
| \(\epsilon\) \(\times 10^9\) | \(-7.7.4 (64)\)   |
| \(\epsilon\) \(\times 10^9\) | \(-2.3.12 (62)\)  |
| \(\epsilon\) \(\times 10^9\) | \(-6.89 (83)\)    |
| \(\epsilon\) \(\times 10^9\) | \(-1.2.93 (27)\)  |
| \(C_{10}\)                  | \(-7.14 (123)\)    |
| \(\alpha_{NO}(N)\)         | \(-1.73.05 (101)\) |
| \(\alpha_{NO}(N)\)         | \(-3.56 (109)\)    |
| \(\alpha_{NO}(N)\)         | \(-9.87 (171)\)    |
| \(\alpha_{NO}(N)\)         | \(-2.06.12 (70)\)  |
| \(\epsilon\) \(\times 10^3\) | \(-1.43 (45)\)    |
| \(\epsilon\) \(\times 10^3\) | \(-3.02 (163)\)   |
| \(\epsilon\) \(\times 10^3\) | \(-3.27 (23)\)    |

\(^a\) Numbers in parentheses are 1σ uncertainties in units of the least significant figures.

Table 5: Derived spectroscopic parameters\(^a\) (MHz) of NO from the isotopic invariant fit.

| Parameter          | Value              |
|--------------------|--------------------|
| \(Y_{01}\)         | 51.111.184.2 (11)  |
| \(\Delta N\)       | \(-2.23.66 (147)\) |
| \(\Delta N\)       | \(-2.26.99 (156)\) |
| \(Y_{02} \times 10^3\) | \(-1.63.89 (45)\)  |
| \(N\)              | \(-7.96 (37)\)     |
| \(A_{00}\)         | 3.695.477.03 (21)  |
| \(A_{NO}\)         | 1.416 (18)         |
| \(A_{NO}\)         | 1.323 (30)         |
| \(p_{10}\)         | 3.50.606 (29)      |
| \(p_{NO}\)         | \(-1.24.68 (68)\)  |

\(^a\) Numbers in parentheses are 1σ uncertainties in units of the least significant figures.

has residuals on average much larger than 1.0. Among the smallest values are \(\Delta\) doubling transitions from Refs. [14, 15]. The rms error of our \(^{15}\)O data is 0.871, slightly better for the pure rotational data and slightly worse for the FS data.

4. Discussion and conclusion

We have reproduced extensive rotational data of several NO isotopologs along with heterodyne IR data in one isotopic invariant fit. The later inclusion of extensive rovibrational data may affect some parameters outside the present uncertainties. Moreover, additional vibrational and possibly BO corrections will be required for some parameters. The NO \(v = 1 \rightarrow 0\) energy difference, in particular, is merely a fitting parameter at present.

The hyperfine parameters, however, will not be affected by additional IR data because of the lower accuracy of the data and because HFS is not resolved in the FTS data. Contributions to the interpretation of the NO HFS parameters have been provided numerous times, e.g., in Refs. [3, 9, 60, 61]. The \(^{14}\)N HFS parameter of NO and NS are quite similar [61] with the ones of NS being consistently smaller [61, 62], hence the spin density is smaller at N in NS compared to NO.

An early RF study yielded a value \(eQ_{LO} = -21\) kHz with rather small uncertainty of less than 2 kHz [11], not in agreement with our value of \((-6.89 \pm 0.83)\) kHz, whereas an extended update of that RF study yielded \((-9 \pm 8)\) kHz [13]. The parameter \(eQ_{LO}\) was also determined, e.g., for BrO [46]. If we scale that value of \((-21.817 \pm 0.087)\) MHz with the NO/BrO ratios of \(A_{NO}\) and \(eQ_{LO}\), we obtain a value of \(-7.97\) kHz, rather close to our NO value. The agreement should not be overinterpreted because deriving \(eQ_{LO}\) values of ClO and IO analogously from the BrO value yields 0.96 MHz and 141 MHz compared to experimental values of \((0.313 \pm 0.071)\) MHz [63] and \((198.17 \pm 0.65)\) MHz [64], respectively.

The values \(v = -181.15\) MHz and \(A_D = 0.169\) MHz, derived from Zeeman spectroscopy of NO [43], and our values of \(\gamma_{00} = -193.4\) MHz or \(\gamma = -189.7\) MHz in \(v = 0\) and
$A_D = 0.123$ MHz are in reasonable accordance. No uncertainties were quoted in the Zeeman study. But even if uncertainties were determined, it would be difficult to judge which values are more reliable. A combination of both methods should yield improved values. Both results demonstrate that fitting $\gamma$ in rotational or rovibrational spectra of NO isotopologs is more appropriate than fitting $A_D$ even though the ratio $A_D/A$ is small with respect to $D/B$ if $\gamma$ is omitted from the fit.

An isotopic invariant fit of rotational data of three NO isotopologs was carried out earlier [7]. Their values, $A_0^N = -2.265$ (61) and $A_0^O = -2.345$ (34), compare very favorably with ours, $A_0^N = -2.2317$ (15) and $A_0^O = -2.2970$ (16). Our uncertainties are considerably smaller because of extensive additional data for NO and $^{15}$NO from the present study, and data for $^{17}$O and $^{18}$O from the present study.

The available BOB parameters $A_{01}$ and $A_{02}$ of NO are compared in Table 6 with data of related diatomics. There are three contributions to $A_{01}$ [47]: (i) a higher-order semiclassical term that originates in the Dunham formalism and is usually very small, (ii) a diabatic (or nonadiabatic) term that is proportional to the molecular $g$-value $g_J$, and finally, (iii) an adiabatic term that is derived from the experimental $A_{01}$ value by subtracting the two former contributions. The latter contribution appears to depend more on the two atoms in a given diatomic molecule than on specifics of this molecule [69]. The second contribution is usually the dominant one, and its magnitude is particularly large if there exist low-lying electronic states of the same spin-multiplicity in the molecule [47].

The similarity of the NO and CO values should not be over-interpreted because values for, e.g., CO$^+$ are quite different: $A_{01}^C = -0.224$ (14) and $A_{01}^O = -1.033$ (33) [70]. The $A_{01}$ values in Table 6 cover a considerable part of the normal values, and trends are hard to detect. The magnitudes of the NS values are comparatively large for a diatomic consisting of fairly light atoms, indicative of at least one fairly low lying electronic doublet state [47, 62]. However, these values are still much smaller in magnitude than those of CH$^+$, $A_{01}^C = -7.9749$ (105) and $A_{01}^H = -9.2263$ (76) [52].

The BOB parameters $A_{01}$ appear to be usually negative and increasing in magnitude with $i$, as in the case of AlH [71] or, with more limited values, CH$^+$ [52]. As can be seen in Table 6 this is also the case for $A_{02}^A$ of CO and NO. In addition, it appears as if the poorly determined $A_{02}$ values of CS are of correct order of magnitude. The remaining BOB parameters determined for NO, $A_{01}^N$, $A_{01}^O$, and $A_{01}^C$ are all of fairly small magnitude.

Predictions of the rotational spectra of several NO isotopologs will be available in the catalog section [1] of the CDMS [39, 40]. The line, parameter, and fit files from the isotopic invariant fit are deposited as supplementary material. In addition, these files, along with other auxiliary files, will be available in the fitting spectra section [2] of the CDMS.

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### Appendix A. Supplementary Material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/msa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi: .

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1. http://www.astro.uni-koeln.de/cdms/
2. http://www.astro.uni-koeln.de/site/vorhersagen/pickett/beispiele/NO/

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Table 6: Comparison of Born-Oppenheimer breakdown parameters $A_{01}$ and $A_{02}$ of NO with those of related molecules.

|       | NO$^N$ | NS$^N$ | CO$^C$ | CS$^C$ | SiO$^O$ | SiS$^O$ | O$_3$ | SO$^O$ |
|-------|--------|--------|--------|--------|---------|---------|-------|--------|
| $A_{01}^N$ | -2.2317 (15) | -3.424 (68) | -2.05603 (24) | -2.5434 (49) | -1.2976 (44) | -1.3935 (42) | -1.7353 (31) | -1.830 (56) |
| $A_{02}^N$ | -6.96 (37) | -6.3978 (20) | -4.9 (57) |
| $A_{01}^O$ | -2.2970 (16) | -2.856 (96) | -2.09934 (24) | -2.3945 (34) | -2.0507 (16) | -1.8728 (55) | -1.7353 (31) | -2.700 (24) |
| $A_{02}^O$ | -11.0 (66) |

$^a$ Numbers in parentheses are 1σ uncertainties in units of the least significant figures.

$^b$ Ref. [62].

$^c$ Ref. [54].

$^d$ Ref. [63].

$^e$ Ref. [46].

$^f$ Ref. [65].

$^g$ Ref. [47].

$^h$ Ref. [53]; value for $X^3\Sigma$; $a^1\Delta_c$: $-1.9144$ (56), $b^1\Sigma_c^+$: $-2.1333$ (74).

$^i$ Ref. [58].
