Global empirical potentials from purely rotational measurements

Nikesh S. Dattani,1,2∗ L. N. Zack,3 Ming Sun,4 Erin R. Johnson,5 Robert J. LeRoy,6 L. M. Ziurys7
1Physical and Theoretical Chemistry Laboratory, Department of Chemistry, Oxford University, OX1 3QZ, Oxford, UK,
2Quantum Chemistry Laboratory, Department of Chemistry, Kyoto University, 606-8502, Kyoto, Japan,
3Department of Chemistry, Wayne State University, 48202, Detroit, Michigan, USA,
4College of Electronic and Optoelectronic Technology, Nanjing University of Science and Technology, 210094, Nanjing, China,
5Chemistry and Chemical Biology, School of Natural Sciences, University of California, Merced, 95343, Merced, California, USA,
6Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Waterloo, N2L 3G1, Waterloo, Ontario, Canada, and
7Department of Chemistry, University of Arizona, 85721, Tucson, Arizona, USA.

The recent advent of chirped-pulse FTMW technology has created a plethora of pure rotational spectra for molecules for which no vibrational information is known. The growing number of such spectra demands a way to build empirical potential energy surfaces for molecules, without relying on any vibrational measurements. Using ZnO as an example, we demonstrate a powerful technique for efficiently accomplishing this. We first measure eight new ultra-high precision (±2 kHz) pure rotational transitions in the X-state of ZnO. Combining them with previous high-precision (±50 kHz) pure rotational measurements of different transitions in the same system, we have data that spans the bottom 10% of the well. Despite not using any vibrational information, our empirical potentials are able to determine the size of the vibrational spacings and bond lengths, with precisions that are more than three and two orders of magnitude greater, respectively, than the most precise empirical values previously known, and the most accurate ab initio calculations in today’s reach. By calculating the \( C_{6} \), \( C_{8} \), and \( C_{10} \) long-range constants and using them to anchor the top of the well, our potential is globally in excellent agreement with ab initio calculations, without the need for vibrational spectra and without the need for any data in the top 90% of the well.

Measuring and assigning microwave spectra is now easier than ever. Plenty of systems are having high-resolution spectra recorded for the first time, and in many of these systems it is only the pure rotational transitions that are available ([1], [2], [3], and [4], just to name a few). Outstanding examples of recent studies for which measurements of pure rotational spectra have been made include PbCl and PbF which are at sharp focus in the investigation of the electron electric dipole moment for ruling out alternatives to the Standard Model [5, 6, [7]; and the open-shell diatomic SnI whose spectrum was previously considered too challenging to study [8]. Furthermore, chirped-pulse FTMW technology now promises the emergence of yet another wave of new pure rotational spectra, demanding techniques for extracting the most information from experiments in the absence of vibrational information.

Among the long list of systems for which only pure rotational data is available, one example that has wide-ranging applications across physics is ZnO. Condensed- and gas-phase studies of zinc oxide based materials have been under intense focus for several decades [9, 10]. ZnO has a wide band gap (\( \sim 3.4 \) eV) and a large exciton binding energy (\( \sim 60 \) meV) [9], making it an attractive material for many industrial applications. Bulk ZnO is often used as a semiconductor and can be doped with other materials to enhance functionality. Many of these properties make ZnO a more advantageous choice than GaN, for example, in components for optoelectronics, electronic circuits, and spintronics. High electromechanical coupling constants and robustness also make ZnO-based materials a popular choice for a large variety of nanostructures. ZnO has become the subject of an enormous number of experimental and theoretical studies, and has been surveyed extensively in several recent reviews [9, 10].

However, despite this extensive amount of work on ZnO, there has been some hesitation to experimentally study the ZnO monomer. Diatomic oxides of 3d transition metals are very important for astrophysics and high-temperature chemistry and consequently have received plenty of attention from theoreticians and experimentalists [11]. Contrarily, Zinc has often been neglected from such laboratory studies on d-block metal oxides because it has completely filled subshells and thus is not a true transition metal [12]. Additionally, the metal’s low electron affinity and high ionization potential seem to indicate that it would not be reactive with other atoms, molecules, or ligands. Spectroscopic studies of the ground \( X(1\Sigma^{+}) \) electronic state of monomeric ZnO thus far are limited to merely one high-resolution study [13], where only rotational information for was obtained, and even this was only for \( J \geq 8 \) and for just the lowest 5 out of scores of vibrational states. With over 90% of the potential completely unexplored, and a sheer lack of vibrational information, the ambition to build a global empirical potential all the way up to dissociation would seem arduous if at all possible, and furthermore, the data in [13] started from a rotational level of \( J = 8 \), ruling out the possibility to obtain even a rotationless potential.

In this Letter we report new measurements of the \( J(1 \rightarrow 0) \) transitions for isotopologues of the ZnO X-state covering all stable isotopes of Zn with nuclear
Figure 1. Comparison of our empirical potential with ab initio points based on Ref. [14], and with the long-range theory based on the $C_m$ coefficients calculated in this work and damping functions $D_m(r)$ as defined in Ref. [15]. The global potential is accurate over a broad range of internuclear distances, despite the data only covering $\sim 10\%$ of the well, and being only pure rotational transitions.

Table I. Summary of the new transition energies measured in this work (in MHz), and their uncertainties.

| $v$ | $J'$ | $J''$ | $^{64}$Zn$^{16}$O | $^{66}$Zn$^{16}$O | $^{68}$Zn$^{16}$O | $^{70}$Zn$^{16}$O | Unc. |
|-----|-----|-----|------------------|------------------|------------------|------------------|-----|
| 0   | 1   | 0   | 27072.788       | 26909.031        | 26754.756        | 26609.181        | $\pm 2$ kHz |
| 1   | 1   | 0   | 26843.893       | 26682.213        | $-$              | $-$              | $\pm 2$ kHz |
| 2   | 1   | 0   | 26615.559       | $-$              | $-$              | $-$              | $\pm 2$ kHz |
| 3   | 1   | 0   | 26387.293       | $-$              | $-$              | $-$              | $\pm 2$ kHz |

spin 0. Our new data span various vibrational states in the range $v = 0 - 3$, and our measurements are more than an order of magnitude more precise than the measurements of the much higher rotational levels reported in [13]. Early attempts to build an accurate global potential from purely rotational data go back to as early as 1995 when Grabow et al. fitted various potential function models to microwave spectra of NeAr [16]. However, the only potential function models available at the time were very primitive and different models gave very different potentials. In 2006, and again in 2008, Grabow and co-workers demonstrated improved pursuits in this endeavor in a series of excellent papers on on Se- and Te-based diatomics [17], and while the models used there were more sophisticated, those potentials do not extrapolate well beyond the data region since these Morse-like models do not have the correct long-range behavior built in. In 2010 one of us (RJL) compared the well depths predicted by global potentials based only on microwave data for $v = 0$ to those using all data available, but the full potentials and other predicted properties such as the vibrational spacing were not compared at that time [18].

With the new measurements in this work, and a clever choice of a potential function model that intrinsically promises to yield the correct behavior in much of the region where data is absent, we are able to build analytic potentials which are robust globally from the bottom of the well to the dissociation limit. For each isotopologue, our potentials reproduce all experimental transition data with an overall standard deviation well below the experimental uncertainties, and also match well with state of the art ab initio calculations from a recent comprehensive study [14]. Our potentials allow us to make various predictions that were unattainable previously.

The experiments. The spectra were measured using a Balle-Flygare type Fourier-Transform microwave spectrometer, described in detail in [19]. The instrument consists of a Fabry-Perot cavity formed from two spherical aluminum mirrors arranged in a near confocal arrangement. Microwave radiation is injected into the cavity via an antenna embedded in one mirror, and molecular emission is detected by an antenna in the opposite mirror. The signals are recorded in the time domain and are fast Fourier transformed to generate a frequency-domain spectrum. Each transition appears as a Doppler doublet and the transition frequencies are reported as the average
of the two Doppler components.

ZnO was synthesized from the reaction of zinc metal vapor and 0.5% N₂O in argon in a discharge assisted laser ablation source [24]. The metal vapor was generated by ablating a rotating/translating zinc rod with the second harmonic (532 nm) of a Nd:YAG laser (100 mJ/5 ns pulse). The gas mixture was introduced into the cavity by a pulsed valve operating at a 10 Hz rate, entraining the metal vapor before application of a DC discharge (1.0 kV, 30–50 mA). The molecular beam was oriented at a 40° angle relative to the optical axis, and the ablation laser was introduced perpendicular to the supersonic jet. The new transition energy measurements are presented in Table I.

Adding our new measurements from Table I to the complete set of high-resolution spectra measured thus far for ZnO, yields the final dataset presented in Table II.

The potential energy function. The MLR (Morse/Long-range) model for potential energy functions [15, 25] is particularly pertinent when working with very limited data. In 2011 an analytic potential was built for a molecular state with an extremely limited dataset [26], where it was shown that for the \((1^3\Sigma_g^+)\)-state of Li₂, the MLR model made it possible to bridge a gap of more than 150 THz (\(> 5000 \text{ cm}^{-1}\)) between data at the very bottom of the well and data extremely close to the dissociation limit, with a function that was analytic globally. In 2013, high-resolution measurements showed that predictions made by that MLR potential, for the energies in the middle of this gap of more than 5000 cm\(^{-1}\), were correct to about 1 cm\(^{-1}\) [27]. A more extreme example was performed very recently for the \(b^1Π_u\)-state of Li₂, for which the region of the potential that had been experimentally unexplored was roughly the same size as in the case of the \(c\)-state, except that rather than bridging a gap between data near the bottom and data near the top of the well, only data at the bottom of the well was available [28]. Nevertheless, it was still possible to build an analytic MLR potential for this state that reproduced the available data at the very bottom of the well, while also achieving the correct long-range behavior at the dissociation limit.

The present case of the \(X\)-state of ZnO is a much more challenging case. Two reasons are (1) the extrapolation from the data region to the dissociation limit is nearly 1 PHz large, and (2) with only pure rotational data, no vibrational information is available. In this work we overcame these challenges by calculating accurate long-range potential terms, and incorporating them into a carefully selected MLR function. As shown in [25], all MLR models have the property:

\[
\lim_{r \to \infty} V_{\text{MLR}}(r) = \mathcal{D}_c - u_{\text{LR}}(r) + \mathcal{O}\left(\left(u_{\text{LR}}(r)^2\right) + \cdots\right), \quad (1)
\]

in which \(\mathcal{D}_c\) is the dissociation energy and the long-range function \(u_{\text{LR}}(r)\) is chosen so that Eq. 1 represents the correct theoretical long-range behavior of the function. For the \(X\)-state of ZnO, we choose

\[
u_{\text{LR}} = \frac{C_6 D_6(r)}{r^6} + \frac{C_8 D_8(r)}{r^8} + \frac{C_{10} D_{10}(r)}{r^{10}}, \quad (2)
\]

in which \(D_m(r)\) are damping functions, as defined in [15] to take into account electron wavefunction overlap which is not accounted for by \(C_m\) constants alone. Upon insertion into Eq. 1 gives (note \(\lim_{r \to \infty} D_m(r) = 1\) for all \(m\)):

\[
\lim_{r \to \infty} V_{\text{MLR}}(r) = \mathcal{D}_c - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} \cdots. \quad (3)
\]

At present, long-range coefficients for ZnO are only known for bulk ZnO. Therefore, in this work we calculate \(C_6\), \(C_8\) and \(C_{10}\) for Zn\((1^1S) + O(1^1D)\), which is the unbound state to which the \(X\)-state of ZnO dissociates. We use the exchange-hole dipole moment (XDM) model [29, 30], which is a model of dispersion based on second-order perturbation theory. The key feature of XDM is that the source of the instantaneous dipole moments responsible for the dispersion interaction is taken to be the dipole moment of the exchange hole. The dispersion coefficients \((C_m)\) are then given in terms of the multipole moments of the exchange hole, \((M^2)\) (\(\ell = 1, 2 \ldots\) for dipole, quadrupole, etc. moments), and the atomic polarizabilities, \(\alpha\). For \(C_6\), \(C_8\) and \(C_{10}\), the resulting formulas are given in Eqs. 4 to 6 for any atoms \(i\) and \(j\), in this case Zn and O. In practice, the Becke-Roussell model of the exchange hole [31] is used in XDM calculations as it allows straightforward evaluation of the moments from local properties of the electron density. The interested
Comparison of some physical quantities derived from our potential, to previous published values.

\( r_c \) \( \AA \) \( ^{64}\text{Zn}^{16}\text{O} \) 1.7046145 ± 0.000002 1.7047 ± 0.0002 – – – –
\( ^{66}\text{Zn}^{16}\text{O} \) 1.7046151 ± 0.000002 1.7047 ± 0.0002 – – – –
\( ^{67}\text{Zn}^{16}\text{O} \) 1.7046154 ± 0.000002 1.7047 ± 0.0002 – – – –
\( ^{68}\text{Zn}^{16}\text{O} \) 1.7046157 ± 0.000002 1.7047 ± 0.0002 – – – –
\( ^{70}\text{Zn}^{16}\text{O} \) 1.7046162 ± 0.000002 1.7047 ± 0.0002 – – – –

\( E_{v=1} - E_{v=0} \) \( \text{cm}^{-1} \) \( ^{64}\text{Zn}^{16}\text{O} \) 728.395±0.007 – 726 ± 20 770 ± 40 805 ± 40 727

The reader is directed to Ref. [29] for a complete description of the model.

\[
C_6^{ij} = \frac{\alpha_i \alpha_j \left( M_1^2 \right)_i \left( M_1^2 \right)_j}{\left( M_1^2 \right)_i \alpha_i + \left( M_1^2 \right)_j \alpha_j}, \quad (4)
\]

\[
C_8^{ij} = \frac{3 \alpha_i \alpha_j \left( \left( M_1^2 \right)_i \left( M_2^2 \right)_j + \left( M_2^2 \right)_i \left( M_2^2 \right)_j \right)}{2 \left( M_1^2 \right)_i \alpha_j + \left( M_2^2 \right)_i \alpha_i}, \quad (5)
\]

\[
C_{10}^{ij} = \frac{2 \alpha_i \alpha_j \left( \left( M_1^2 \right)_i \left( M_2^2 \right)_j + \left( M_2^2 \right)_i \left( M_2^2 \right)_j \right)}{\left( M_1^2 \right)_i \alpha_j + \left( M_1^2 \right)_j \alpha_i} + \frac{21}{5} \frac{\alpha_i \alpha_j \left( M_1^2 \right)_i \left( M_2^2 \right)_j}{\left( M_1^2 \right)_i \alpha_j + \left( M_1^2 \right)_j \alpha_i}. \quad (6)
\]

Fully numerical, self-consistent Hartree-Fock calculations were performed for the Zn and O atoms using the NUMOL program [32]. Dispersion coefficients were then calculated from the XDM model using free atomic polarizabilities obtained from Ref. [33]. This approach gives homonuclear \( C_6 \) dispersion coefficients (in atomic units) of 356.5 for diatomic Zn(\( ^1\)S) and 16.14 for diatomic O(\( ^3\)P), in good agreement with the available reference values of 359 [34] and 14.89 [35], respectively. Note that the ground state of ZnO will dissociate to give an O(\( ^1\)D) atom and the Zn–O dispersion coefficients were calculated using the lowest-energy single Slater-determinant reference state for oxygen. The atomic polarizability of O(\( ^1\)D) was taken to be 5.492 au by correcting the experimental polarizability with the calculated difference between singlet and triplet results [36]. Our final XDM dispersion coefficients for ZnO, in atomic units, are \( C_6 = 71.34, C_8 = 2927 \) and \( C_{10} = 1.368 \times 10^5 \).

Computational details and results. We use the diatomic Hamiltonian model of [25], with the potential energy function corresponding to the primary isotopologue \( ^{64}\text{Zn}^{16}\text{O} \) and represented by the MLR model (described in the previous section of this Letter). The potentials for all other stable isotopologues are represented by adding Born-Oppenheimer breakdown (BOB) corrections to the \( ^{64}\text{Zn}^{16}\text{O} \) potential – we use the BOB functions of [25]. The final potentials and BOB correction functions were calculated by a direct-potential-fit (DPF) to all high-resolution spectroscopic transitions of gas-phase ZnO measured thus far, as depicted by the dataset summary of Table II. The parameters of the potentials and BOB correction functions were obtained by a least squares fit of the eigenvalues of the Hamiltonian, to the measured transition energies. These measured energies are reproduced by our fits to well within their experimental uncertainties. All DPF calculations were performed with a freely available program \textsc{DPotFit2.0}, and further computational details are described in the program’s user manual [37]. The parameters defining our final recommended MLR function and BOB correction function parameters are listed in Table IV. Fig. 1 displays this recommended potential graphically, and Table III compares physical quantities derived from our potential, to values obtained in previous papers.

Conclusion. We have demonstrated a technique for building global empirical potentials using only (very little) pure rotational data, and our application to gas-phase ZnO has engendered some compelling results. Without vibrational information, our empirical potential was able to predict the vibrational energy spacing correctly, and with more than three orders of magnitude higher precision than the best experimental measurements and \textit{ab initio} calculations to date. Our empirical potential which was based on only data spanning only about ∼10% of the well, was in excellent agreement with \textit{ab initio} calculations over a significantly larger portion of the experimentally unexplored well. We strongly encourage the use of this technique for making the most of pure rotational spectra, and we anticipate it becoming an important tool for microwave spectroscopy.

Acknowledgments. We would like to thank Dr. Nick Walker of Newcastle University for informing us about one of the main selling points of our method. NSF thanks JSPS and Yoshitaka Tanimura for generous hospitality, RJL thanks NSERC/CRSNG, and LMZ acknowledges NSF Grant CHE-1057924 for financial support.

[1] C. Pérez, S. Lobsiger, N. A. Seifert, D. P. Zaleski, B. Temelso, G. C. Shields, Z. Kisiel, and B. H. Pate, Chemical Physics Letters 571, 1 (2013).
[2] C. C. Womack, K. N. Crabtree, L. McCaslin, O. Mar-
Table IV. Parameters defining our recommended MLR potential for the X-state of $^{64}$Zn$^{64}$O and the BOB correction functions for $^{64}$Zn$^{64}$O and all the other stable isotopologues. Parameters in square brackets were held fixed in the fit, while numbers in round brackets are 95% confidence limit uncertainties in the last digit(s) shown. The potential also incorporates damping functions according to [15], with $s = -2$ and $\rho = 0.88$.

| Parameter | Value | Units |
|-----------|-------|-------|
| $D_0$ cm$^{-1}$ | 29979.25 | | [29979.25] |
| $r_c$ Å | 1.704682(2) | | u$_{Zn}^0$ cm$^{-1}$ | -1.2(4) |
| $C_6$ a.u. | 71.34 | | u$_{Zn}^0$ cm$^{-1}$ | 0.0 |
| $C_8$ a.u. | 2927 | | | |
| $\rho$ | 1.368 x 10$^5$ | | | |
| $\{p, q\}$ | (25, 4) | | $\{p_{max}, q_{max}\}$ | (3, 3) |
| $\rho_{ref}$ Å | 1.75 | | $t_{8a}^{0}$ | 0.0 |
| $1 \times 10^{-3}$ | 0.05138913 | | $t_{8a}^{0}$ | -0.0010 |
| $1 \times 10^{-3}$ | 16.182591 | | $t_{8a}^{0}$ | 0.0 |
| $1 \times 10^{-3}$ | 100.57037 | | $t_{8a}^{0}$ | 0.0 |
| $1 \times 10^{-3}$ | 423.085 | | $t_{8a}^{0}$ | 0.0 |
| $1 \times 10^{-3}$ | 1345.81 | | $t_{8a}^{0}$ | 0.0 |
| $1 \times 10^{-3}$ | 3509.31 | | $t_{8a}^{0}$ | 0.15 |
| $1 \times 10^{-3}$ | -8573.9 | | $t_{8a}^{0}$ | 0.9 |
| $1 \times 10^{-3}$ | 2062.4 | | $t_{8a}^{0}$ | 0.1 |
| $1 \times 10^{-3}$ | -3637.0 | | $t_{8a}^{0}$ | 0.0 |
| $1 \times 10^{-3}$ | -2.87 x 10$^4$ | | $t_{8a}^{0}$ | 0.0 |

[1] W. B. Jensen, Journal of Chemical Education 80, 952 (2003).
[2] D. P. Zaleski, H. Kockert, S. L. Stephens, N. Walker, L. M. Dickens, and C. Evans, in 69th International Symposium on Molecular Spectroscopy (2014) p. W114.
[3] D. P. Zaleski, H. Kockert, S. L. Stephens, N. Walker, L. M. Dickens, and C. Evans, in 69th International Symposium on Molecular Spectroscopy (2014) p. RE08.
[4] U. Özgu, Y. I. Aliev, A. Tekes, E. A. Reschikov, S. Dogan, V. Avrutin, S.-J. Cho, and H. Morkoc, Journal of Applied Physics 98, 041301 (2005).
[5] Y. Gong, M. Zhou, and L. Andrews, Chemical reviews 109, 6765 (2009); H. Oymak and S. Erikc, International Journal of Modern Physics B 26, 1230003 (2012).
[6] A. J. Merer, Annual Review of Physical Chemistry 40, 407 (1989); C. Barnbaum, A. Omont, and M. Morris, Astronomy and Astrophysics 310, 259 (1996); R. Tylenda, L. A. Crause, S. K. Górný, and M. R. Schmidt, ibid. 439, 651 (2005).
[7] L. W. Qiao, P. Li, and K. T. Tang, Journal of Chemical Physics 130, 044309 (2009).
[8] V. D. Moravec, S. A. Klopiec, B. Chatterjee, and C. C. Jardool, Chemical Physics Letters 341, 313 (2001).
[9] J. H. Kim, X. Li, L.-S. Wang, H. L. de Clercq, C. A. Fancher, O. C. Thomas, and K. H. Bowen, The Journal of Physical Chemistry A 105, 5709 (2001).
[10] C. A. Fancher, H. L. de Clercq, O. C. Thomas, D. W. Robinson, and K. H. Bowen, The Journal of Chemical Physics 109, 8426 (1998).
[11] M. Waalschijlker and H. Partridge, The Journal of Chemical Physics 109, 8430 (1998).
[12] M. Sun, D. T. Haflen, J. Min, B. Harris, D. J. Clouthier, and L. M. Ziurys, The Journal of Chemical Physics 133, 174301 (2010).
[13] R. J. Le Roy, N. S. Dattani, J. a. Coxon, A. J. Ross, P. Crozet, and C. Linton, The Journal of Chemical Physics 131, 204309 (2009).
[14] N. S. Dattani and R. J. Le Roy, Journal of Molecular Spectroscopy 268, 199 (2011).
[15] M. Semczuk, X. Li, W. Gunton, M. Haw, N. S. Dattani, J. Witz, A. K. Mills, D. J. Jones, and K. W. Madison, Physical Review A 87, 052505 (2013).
[16] N. S. Dattani and R. J. Le Roy, To appear (2014).
[17] A. D. Becke and E. R. Johnson, The Journal of Chemical Physics 127, 154108 (2007).
[18] A. Otero-de-la Roza and E. R. Johnson, J. Chem. Phys. 138, 204109 (2013).
[19] A. D. Becke and M. R. Roussel, Phys. Rev. A 39, 3761 (1989).
[20] A. D. Becke and R. M. Dickson, The Journal of Chemical Physics 92, 3610 (1990).
[21] D. R. Lide and W. M. Haynes, eds., CRC handbook of chemistry and physics, 90th edition (CRC Press, 2010).
[22] L. W. Qiao, P. Li, and K. T. Tang, Journal of Chemical Physics 137, 084309 (2012).
[23] D. J. Margoliash and W. J. Meath, Journal of Chemical Physics 68, 1426 (1978).
[24] M. M., P. W. Fowler, and J. M. Hutson, Molecular Physics 98, 453 (2000).
[25] R. J. Le Roy, J. Y. J. Seto, and Y. Huang, “DPotFit 2.0: A Computer Program for Fitting Diatomic Molecule Spectra to Potential Energy Functions (University of Waterloo Chemical Physics Research Report CP-667).” (2013).