A Method for the Variational Calculation of Hyperfine-Resolved Rovibronic Spectra of Diatomic Molecules

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ABSTRACT: An algorithm for the calculation of hyperfine structure and spectra of diatomic molecules based on the variational nuclear motion is presented. The hyperfine coupling terms considered are Fermi-contact, nuclear spin-electron spin dipole–dipole, nuclear spin–orbit, nuclear spin–rotation, and nuclear electric quadrupole interactions. Initial hyperfine-unresolved wave functions are obtained for a given set of potential energy curves and associated couplings by a variation solution of the nuclear-motion Schrödinger equation. Fully hyperfine-resolved parity-conserved rovibronic Hamiltonian matrices for a given final angular momentum, $F$, are constructed and then diagonalized to give hyperfine-resolved energies and wave functions. Electric transition dipole moment curves can then be used to generate a hyperfine-resolved line list by applying rigorous selection rules. The algorithm is implemented in DUO, which is a general program for calculating spectra of diatomic molecules. This approach is tested for NO and MgH, and the results are compared to experiment and shown to be consistent with those given by the well-used effective Hamiltonian code PGOPHER.

1. INTRODUCTION

The hyperfine structure of molecules lays the foundation for the studies of many important areas. The most immediate application is to reveal the properties of the molecules.1–3 Other examples include laser cooling experiments,4,5 astronomical observations,6 and, of course, nuclear magnetic resonance which has many applications including ones in medicine.

In the absence of external fields, the rotational hyperfine structure results from interactions between the electric and magnetic multipole moments of the nuclei and their molecular environments.7 Due to parity conservation inside the nuclei, only even electric and odd magnetic multipoles are non-vanishing. Although higher multipole effects are observed in some experiments, the dominant contributions to the hyperfine structure arise from magnetic dipole and electric quadrupole interactions.

Frosch and Foley8 performed a pioneering theoretical study of the magnetic interactions between nuclei and electron spins in diatomic molecules based on the Dirac equation, see discussion by Brown and Carrington.9 Bardeen and Townes10 provided the first extensive discussion of the electric quadrupole interactions.

The application of irreducible spherical tensor operators facilitates the evaluation of effective hyperfine Hamiltonian matrix elements,9,11–13 although one must still pay attention to anomalous commutation relationships when coupling angular momenta.14,15 Standard practice is to use these matrix elements to solve problems for which hyperfine structure is important using effective Hamiltonians which implicitly use a perturbation-theory-based representation of the problem.3,6

The effective Hamiltonian of a fine or hyperfine problem is usually constructed within a particular vibrational state, and the rotational coupling terms are treated as perturbations. The assumptions implicit in this approach are usually valid because the splitting of the (rotational) energy levels due to hyperfine effects are generally small compared to the separation between electronic or vibrational states. However, this assumption can fail, such as for example, for Rydberg states of molecules.16,17

The $\text{B} \ ^1\Pi \rightarrow \text{C} \ ^3\Pi$ avoided crossing structure in NO is another example of strong electronic state interaction. The perturbative treatment of this vibronic coupling is difficult: it requires a lot of parameters,18 and is not very accurate. The interaction between different states leads to significant complications which are difficult to model using the standard effective Hamiltonian approach.

In contrast, our recent work on a spectroscopic model for the four lowest electronic states of NO19 proposed a compact solution for the problem based on the use of a variational method to treat the nuclear motion. In our approach, which is

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based on the use of potential energy curves and appropriate couplings, it was only necessary to introduce one potential energy coupling curve between the coupled B^2Π and C^2Π electronic states; this gave an accurate rovibronic line list for NO.20 These calculations used a general program for the calculation of spectra of diatomic molecules, DUO.21 DUO is a variational nuclear motion program developed for the calculation of rovibronic spectra of diatomic molecules as part of the ExoMol project.22 It provides explicit treatment of spin–orbit and other coupling terms and can generate high-accuracy fine-structure diatomic line lists. DUO has been used to generate many line lists including those for AlO,23 CaO,24 VO,25 TiO,26 YO,27 and SiO,28 which are provided via the ExoMol database.29 DUO was also recently employed to calculate temperature-dependent photodissociation cross sections and rates.30 DUO has also been adapted to treat...
ultralow energy collisions as the inner region in an R-matrix formalism,\textsuperscript{31} hyperfine effects are very important in such collisions. Recently, a new module treating electric quadrupole transitions has been added to DUO,\textsuperscript{32} which makes it capable of predicting spectra for diatomic molecules with no electric dipole moment, for example O$_2$ and N$_2$. However, up until now DUO had not treated hyperfine effects. In this context we note that hyperfine coupling is particularly strong for VO,\textsuperscript{33,34} meaning that the current ExoMol VO line list, VOMYTE\textsuperscript{25}, which is not hyperfine resolved, is unsuitable for high resolution work, such as the study of exoplanets using high-resolution Doppler-shift spectroscopy.\textsuperscript{35}

Here we present a variational procedure for calculating hyperfine-resolved spectra of diatomic molecules. The new algorithm we design is implemented as new modules in DUO. In general, the most challenging part of solving quantum mechanical problems using a variational method is finding good variational basis sets. We show below that DUO gives appropriate basis sets thanks to its well-designed calculation hierarchy and algorithm. Numerical tests indicates that the algorithm proposed here can achieve high accuracy for the calculation of hyperfine structure.

2. OVERVIEW

In this section, we outline our algorithm so that the readers can easily follow the details given in the following sections. Figure 1 gives a graphical representation of the algorithm.

We write the Hamiltonian for the problem as

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}_{\text{hf}}$$

(1)

where $\mathcal{H}^{(0)}$ is the rovibronic Hamiltonian which DUO originally used to give fine structure resolved solutions for diatomic molecules, and $\mathcal{H}_{\text{hf}}$ gives the nuclear hyperfine interaction terms introduced in this work. We emphasize that although this structure is the standard one used in perturbation theory, here we aim for a full variational solution of the whole Hamiltonian $\mathcal{H}$.

2.1. Rovibronic Fine Structure. DUO has well-developed modules, surrounded by black rectangles in Figure 1, for the calculation of rovibronic energies and wave functions.

The computational procedure used by DUO to obtain solutions for $\mathcal{H}^{(0)}$ is divided into two steps. First, the rotationless Schrödinger equation is solved independently for each uncoupled potential energy curve, $V_{\text{state}}(R)$, to give vibrational energy levels, $E_{\text{state},\nu}$, and wave functions, $\psi_{\text{state},\nu}$.

$$\frac{-\hbar^2}{2\mu} \frac{d^2}{dR^2}\psi_{\text{state},\nu}(R) + V_{\text{state}}(R)\psi_{\text{state},\nu}(R) = E_{\text{state},\nu}\psi_{\text{state},\nu}(R)$$

(2)

where $R$ is the internuclear distance, $\mu$ is the reduced mass of the molecule, "state " and $\nu$ indicate the electronic state and vibrational quantum numbers. DUO employs contracted vibrational basis sets given by $\psi_{\text{state},\nu}$ to define a finite-dimension space.

In the second step, a rovibronic Hamiltonian matrix, corresponding to $\mathcal{H}^{(0)}$, for each specific total angular momentum exclusive of nuclear spin, $J$, and parity, $\tau$, is constructed using a Hund’s case (a) basis set:\textsuperscript{36}:

$$\langle \text{state}, \nu, \Lambda, S, \Sigma, J, \Omega \rangle = \langle \text{state}, \nu, \Lambda, S, \Sigma \rangle \langle \text{state}, \nu \rangle \langle J, \Omega \rangle \langle M_J \rangle$$

(3)

which is decoupled into three parts: (i) the electronic eigenfunction, (ii) the vibrational eigenfunction of eq 2, and (iii) the rotational eigenfunction of a symmetric top. The quantum numbers in eq 3, state, $\nu$, $\Lambda$, $S$, $\Sigma$, $J$, $\Omega$, and $M_J$, correspond to the electronic state, the vibrational eigenstate, the projection of the electron orbital angular momentum $L$ on the molecular axis, the projection of the electron spin angular momentum $S$ on the molecular axis, the projection of $J$ on the molecular axis, and the projection of $J$ on the space-fixed $Z$-axis, respectively. Note that, DUO calculates the spectra of diatomic molecules in field-free environments. Thus, we do not really use $M_J$ to construct the basis set, as the left-hand side of eq 3 indicates. All the angular momenta are quantized to the body-fixed axes.

When evaluating the basis elements using the basis functions of eq 3, the necessary coupling curves are integrated over pairs of vibrational basis functions:

$$\langle \text{state}, \nu | C(R) | \text{state} \rangle \langle \text{state} \rangle \langle \text{state} \rangle$$

(4)

where $C(R)$ can be either a diagonal coupling curve for a particular electronic state or an off-diagonal coupling curve between two states. Supported couplings include electron spin–orbit, electron spin–spin, electron spin–rotation etc.\textsuperscript{1,36}

The basis functions of eq 3 do not have finite parities. DUO uses linear combinations of them to define parity-conserved basis functions:

$$+ \frac{1}{\sqrt{2}} \langle \text{state}, \nu, \Lambda, S, \Sigma, J, \Omega \rangle$$

$$+ \frac{1}{\sqrt{2}} \langle -\Lambda, -S - \Sigma, -J, -\Omega | \text{state}, \nu \rangle$$

$$- \frac{1}{\sqrt{2}} \langle \text{state}, \nu, \Lambda, S, \Sigma, J, \Omega \rangle$$

(5)

$$- \frac{1}{\sqrt{2}} \langle -\Lambda, -S - \Sigma, -J, -\Omega | \text{state}, \nu \rangle$$

where $s = 1$ for $\Sigma^-$ states and $s = 0$ for all other states. Note that the parity is independent of $M_J$. Each matrix of $\mathcal{H}^{(0)}$ constructed using these basis functions can be diagonalized to give rovibronic energy levels and wave functions of a definite $J$ and parity $\tau$. Let $|\psi_n^{\tau,J}\rangle$ be the $n$th eigenfunction corresponding to a given $J$ and parity $\tau$, we have

$$\langle \psi_n^{\tau,J} | | H^{(0)} | \psi_n^{\tau,J} \rangle = \delta_{n,m}E_m^{\tau,J}$$

(6)

where $E_m^{\tau,J}$ is the $m$th eigenvalue.

Thanks to the use of complete angular basis sets and the variational method, the final energies are independent of the coupling scheme used. If there is enough vibrational basis (determined by the users' setup), the choice of Hund's case (a) will give correct results even for cases for which other coupling schemes provide a better zeroth-order approximation.

2.2. Nuclear Hyperfine Structure. We program new DUO modules to accomplish the functions denoted by the red rectangles in Figure 1 for nuclear hyperfine structure calculations. We only consider heteronuclear diatomic molecules with one nucleus possessing nonzero spin in this paper. In this case, nuclear spin, $I$, is coupled with $J$ to give total angular momentum, $F$, that is,

$$F = I + J$$

(7)
To evaluate the matrix elements of $\mathcal{H}_{\text{hfs}}$, we introduce the following primitive basis functions

$$|\text{state}, v, \Lambda, S, \Sigma, J, \Omega, I, F, M_F\rangle = |\text{state}, v, \Lambda, S, \Sigma|\text{state}, v\rangle|\Omega, M_F\rangle|I, F, M_F\rangle$$

where the angular momenta $I$ and $F$ are quantized to the space-fixed axes; $J$ is quantized to both the space-fixed and the body-fixed axes; $L$ and $S$ are quantized to the body-fixed axes. Without an external field, $M_F$ can be omitted:

$$|\text{state}, v, \Lambda, S, \Sigma, J, \Omega, I, F\rangle$$

The basis functions are countable in DUO and thus, can be simply denoted as

$$|k, J, I, F\rangle = |k, j\rangle|J, I, F\rangle$$

where $k$ is a counting number for the basis functions associated with a given $J$. It is an equivalent representation of eq 9 and $|k, j\rangle$ is short for eq 3.

The quantum numbers, $J$, $I$, and $F$, satisfy the triangle inequality:

$$|F - I| \leq J \leq F + I$$

The coupling scheme used is known as Hund’s case (a)\(^8\), and is illustrated in Figure 2. We emphasize that because we use complete angular basis sets, our results are independent of the coupling scheme used and its choice largely becomes one of algorithmic convenience.

To obtain a parity-conserved basis set, we rely on the symmetrization procedure given in eq 5 by making use of the eigenfunctions obtained as solutions of $\mathcal{H}^{(0)}$, $|\psi_{m}^{(0)}\rangle$, to define the basis functions:

$$|\phi_{m}^{(l)}\rangle = |\phi_{m}^{(2)}\rangle|J, I, F\rangle$$

The parity conserved rovibronic basis functions, eq 12, can be represented by the primitive basis functions, eq 9 or eq 10

$$|\phi_{m}^{(l)}\rangle = \sum_{k} \langle k, j|\phi_{m}^{(2)}\rangle|k, j\rangle|J, I, F\rangle$$

where the coefficients, $\langle k, j|\phi_{m}^{(2)}\rangle$, have been obtained when calculating rovibronic fine structure by solving for $\mathcal{H}^{(0)}$. The matrix elements of $\mathcal{H}^{(0)}$ in this basis functions are straightforward

$$\langle \phi_{m}^{(l)}, I, F|\mathcal{H}^{(0)}|\phi_{m}^{(l)}, I, F\rangle = \delta_{m,m'}^{(l)}F_{m}^{(l)}$$

Therefore, constructing the hyperfine-resolved matrix elements

$$\langle \phi_{m}^{(l)}, I, F|\mathcal{H}_{\text{hfs}}|\phi_{m}^{(l)}, I, F\rangle$$

just requires the matrix elements of $\mathcal{H}_{\text{hfs}}$

$$\langle \phi_{m}^{(l)}, I, F|\mathcal{H}_{\text{hfs}}|\phi_{m}^{(l)}, I, F\rangle$$

In practice, we first construct the matrix elements of $\mathcal{H}_{\text{hfs}}$ using the primitive basis functions of eq 9 and then transform to the representation of $\mathcal{H}^{(0)}$ of eq 12 using a basis transformation. The mathematical and physical details are discussed in the next two sections. Before that, we outline the algorithm used to calculate hyperfine-resolved spectra.

As a first step, the hyperfine coupling curves, such as the Fermi contact interaction curves,\(^3^7\) are integrated over the vibrational wave functions. DUO uses these vibrational matrix elements to compute the hyperfine matrix elements within a Hund’s case (a) basis set, eq 9, and constructs a Hamiltonian matrix for each specific total angular momentum, $F$. Next, the matrix, corresponding to $\mathcal{H}_{\text{hfs}}$, is constructed in the representation of eq 12. After this step, the hyperfine matrix elements are parity conserved. Combining the rovibronic energies and hyperfine matrix elements, DUO constructs the complete Hamiltonian matrix, corresponding to $\mathcal{H}$, for each given value of $F$ and $\tau$. Diagonalizing this matrix gives the hyperfine-resolved energy levels and corresponding wave functions in the representation of eq 12. Finally, the eigenfunctions are transformed back to Hund’s case (a)\(^p\) representation of eq 9 as this representation is more convenient to use for hyperfine-resolved intensity calculations, for analysis of wave functions, and to assign quantum numbers to hyperfine states.

3. THE HYPERFINE STRUCTURE HAMILTONIAN

We investigate the field-free hyperfine structure of diatomic molecules in which only one of the nuclei possesses nuclear spin, and consider five nuclear hyperfine terms in this work:

$$\mathcal{H}_{\text{hfs}} = \mathcal{H}_{\text{FC}} + \mathcal{H}_{\text{IL}} + \mathcal{H}_{\text{dip}} + \mathcal{H}_{\text{J}} + \mathcal{H}_{\text{EQ}}$$

They are, respectively, the Hamiltonians of the Fermi contact interaction, the nuclear spin–orbit interaction, the nuclear spin–electron spin dipole–dipole interaction, the nuclear spin–rotation interaction, and the nuclear electric quadrupole interaction. These Hamiltonians have the following definitions:\(^9\)\(^1^3\)

$$\mathcal{H}_{\text{FC}} = \sum_{i} \frac{8\pi}{3} \frac{g_{i} g_{N} \mu_{B} N_{i}}{4\pi} \delta(\tau_{i})I_{i}S_{i}$$

$$\mathcal{H}_{\text{IL}} = \sum_{i} \frac{2\mu_{0}}{4\pi} \frac{I_{i}L_{i}}{r_{i}^{3}}$$

$$\mathcal{H}_{\text{dip}} = \sum_{i} \frac{g_{i} g_{N} \mu_{B} N_{i}}{4\pi} \left[ \frac{S_{i} \cdot I_{i}}{r_{i}^{3}} - \frac{3(S_{i} \cdot \tau_{i})(I_{i} \cdot \tau_{i})}{r_{i}^{5}} \right]$$

$$\mathcal{H}_{\text{J}} = c_{J}(R)I_{i}J_{i}$$

$$\mathcal{H}_{\text{EQ}} = \sum_{i,n} \frac{e^{2}}{4\pi \varepsilon_{0} r_{i}^{2}} \sum_{p} (-1)^{p} C_{i}^{(p)}(\theta_{i}, \phi_{i})C_{i}^{(p)}(\theta_{i}, \phi_{i})$$
The constants, $e$, $g_0$, $\mu_B$, $g_{N(0)}$, $\mu_N$, and $\mu_p$ are the elementary charge, the free electron spin $g$-factor, the electron Bohr magneton, the nuclear spin $g$-factor, the nuclear magneton, and the vacuum permeability, respectively. $I$ is the spin of the nucleus of interest (defined as nucleus 1), $r_i$ is the relative position between the $i$th electron and nucleus 1, $\mathbf{S}_i$ is the spin of the $i$th electron, $L$ is the orbit angular momentum of the $i$th electron, and $\delta(\cdot)$ is the Dirac delta function. In eq 19, we introduce the nuclear spin-rotation interaction constant, $c_i(R)$, which is a function of internuclear distance. Section 8.2.2(d) of Brown and Carrington1 and Miani and Tennyson30 define the nuclear spin-rotation tensor and how it can be reduced to a constant for a diatomic molecule. In eq 20, $C^{(2)}_{ij}(\theta, \phi)$ is the modified rank-2 spherical harmonic:

$$C^{(2)}_{ij}(\theta, \phi) = \frac{4\pi}{3} Y^{(2)}_{ij}(\theta, \phi)$$

(21)

where $Y^{(2)}_{ij}(\theta, \phi)$ is the standard spherical harmonic; $(r_i, \theta_i, \phi_i)$ and $(r_j, \theta_j, \phi_j)$ are the positions of the $i$th electron and the $j$th proton, respectively.

The first four hyperfine Hamiltonians, given by eqs 16–19, are nuclear magnetic dipole terms resulting from the interactions between magnetic dipole moment given by nuclear spin and magnetic fields due to the motion of nuclei or electrons. The nuclear electric quadrupole Hamiltonian arises from the interaction between the nuclear electric quadrupole moment and the electric field inside a molecule. The nuclear spin-rotation interaction is usually much weaker than the other four hyperfine terms (if nonzero). See Table 1 of Broyer et al.12 for the order of magnitude of the hyperfine terms. To aid the evaluation of matrix elements, the hyperfine Hamiltonians can be written as scalar products of irreducible tensor operators:9

$$H_F = \sum_i \frac{8\pi}{3} g_0 g_p \mu_B \mu_N \frac{\mu_0}{4\pi} \delta(r_i) T^z(I) \cdot T^z(S_i)$$

(22)

$$H_{II} = \sum_i 2g_N \mu_B \mu_N \frac{\mu_0}{4\pi} T^z(I) \cdot T^z(L_i)$$

(23)

$$H_{dp} = \sum_i -10g_0 g_p \mu_B \mu_N \frac{\mu_0}{4\pi} T^z(I) \cdot T^z(S_i, C^{(2)})$$

(24)

$$H_{ij} = c_i(R) T^z(I) \cdot T^z(J)$$

(25)

$$H_{EQ} = -\epsilon T^z(VE) \cdot T^z(Q)$$

(26)

where $T^z(\cdot)$ indicates a rank-$k$ tensor. All the tensors here are defined in space-fixed frame. The two tensors in eq 26 defining the gradient of electric field and the nuclear quadrupole moment are, respectively:

$$T^z(VE) = -\frac{1}{4\pi e_0} \sum_i \frac{e}{r_i} C^{(2)}(\theta_i, \phi_i)$$

(27)

$$\epsilon T^z(Q) = \epsilon \sum_i r_i^2 C^{(2)}(\theta_i, \phi_i)$$

(28)

4. MATRIX ELEMENTS OF THE HYPERFINE STRUCTURE

4.1. Primitive Matrix Elements of the Hyperfine Structure. In this section, primitive matrix elements of the hyperfine structure are initially evaluated in the representation of eq 9. In this work, we do not consider hyperfine couplings between different electronic states when evaluating primitive matrix elements, which are, thus, diagonal in the electronic state and electron spin, that is,

$$\text{state} = \text{state}', \quad S = S'$$

in the bra-ket notation, and immediately we have

$$|\text{state} \rangle = |\text{state}' \rangle$$

As $F = J + I$, we can initially decouple the representation of $| J, I, F, M_F \rangle$ in eq 8 to uncoupled ones; see Edmonds93 for a formal definition and irreducible spherical tensor operators. Taking the Fermi contact term as an example, the nonvanishing matrix element on the primitive basis functions for $M_F = M'_F$ is

$$(\langle \text{state}, \text{state}, \text{state}, \text{state} | T^1(I) | \text{state}, \text{state}, \text{state}, \text{state} \rangle) = \langle \text{state}, \text{state}, \text{state}, \text{state} | T^1(I) | \text{state}, \text{state}, \text{state}, \text{state} \rangle$$

(29)

where $\{ j_1 \ j_2 \ j_3 \ j_4 \}$ is the Wigner-6j symbol.

The nuclear spin is quantized to the space-fixed axes, and thus, the reduced matrix element of $T^1(I)$ is

$$(\langle \text{state}, \text{state}, \text{state}, \text{state} | T^1(I) | \text{state}, \text{state}, \text{state}, \text{state} \rangle) = \sqrt{I(I+1)(2I+1)}$$

(30)

The electron spin is quantized to the body-fixed axes. To evaluate the second reduced matrix element in eq 29, the electron spin spherical tensor is rotated from the space-fixed frame to the body-fixed frame in which the components of the tensors are denoted by $q$:

$$\langle \text{state}, \text{state}, \text{state}, \text{state} | T^1(I) | \text{state}, \text{state}, \text{state}, \text{state} \rangle = \langle \text{state}, \text{state}, \text{state}, \text{state} | T^1(I) | \text{state}, \text{state}, \text{state}, \text{state} \rangle$$

(31)

where $s$ is the spin of the ith electron in body-fixed system, $D^{(k)}_{ij}(\omega)$ is a Wigner rotation matrix and $\{ j_1 \ j_2 \ j_3 \ j_4 \}$ is a Wigner-3j symbol. The electron tensor operators, $T^1_s(s)$, do not directly act on the electronic part of Hund’s case (a) basis. We may replace the electron spin operators with an effective one:

$$\frac{8\pi}{3} g_0 g_p \mu_B \mu_N \frac{\mu_0}{4\pi} \sum_i \frac{e}{r_i} C^{(2)}(\theta_i, \phi_i)$$

(27)

$$\epsilon \sum_i r_i^2 C^{(2)}(\theta_i, \phi_i)$$

(28)

where $S$ is the total spin. Requiring $\Sigma = \Sigma'$, the Fermi contact interaction curve can be defined as

$$\langle \text{state}, \text{state}, \text{state}, \text{state} | T^1(I) | \text{state}, \text{state}, \text{state}, \text{state} \rangle$$

(32)
where $T^i_s(\Sigma)$ represents the projection operator for each electron $i$ (see eq (7.152) of Brown and Carrington9). On the basis of eqs 29 to 33, we finally get

\[
\sigma(T, \Sigma) = \sqrt{(I+1)}(2I+1) + \sqrt{(2I+1)}(2J+1) \\
\times S(S+1)(2S+1) \\
\times \delta_{\Lambda\Lambda}(\text{state, } \text{state, } \nu

\] where $l$ is the orbital angular momentum of the is electron defined in the body-fixed frame.

The nuclear spin–orbit term, we are only interested in the diagonal matrix elements of $\Lambda$

\[
\langle \text{state, } \text{state, } \nu | l | \text{state, } \text{state, } \nu \rangle = \delta_{\Lambda\Lambda}(\text{state, vld}(R)\text{state, } \nu

\] where $I$ is the orbital angular momentum of the is electron defined in the body-fixed frame.

The diagonal nuclear spin–electron spin dipole–dipole interaction constant curve is defined as37

\[
d(R) = -\sqrt{\delta g_e \mu_e \mu_n} \mu_n \sqrt{\text{state, } \text{state, } \nu

\] where $r$ is the radius of the is electron defined in the body-fixed frame.

To evaluate the matrix elements for the electric quadrupole interaction, we decouple the inner product of second rank irreducible tensors:

\[
\langle \text{state, } \text{state, } \alpha | \Omega | \text{state, } \text{state, } \alpha \rangle

\] which is the nuclear electric quadrupole moment; see Cook and De Lucia39 Appendix 8.4 of Brown and Carrington9. The reduced matrix element of the gradient of electric field is

\[
\langle \text{state, } \text{state, } \nu | \nabla \Omega | \text{state, } \text{state, } \nu \rangle

\]
The diagonal and off-diagonal R-dependent constants of the gradient of electric field are respectively defined as (see eqs (7.159) and (7.163) of Brown and Carrington):  
\begin{equation}
q_d(R) = -2\langle\text{state}, \Lambda, S, \Sigma | \nabla (VE) | \text{state}, \Lambda, S, \Sigma \rangle
\end{equation}
(46)
\begin{equation}
q_s(R) = -2\sqrt{6}\langle\text{state}, \Lambda, S, \Sigma | \nabla (VE) | \text{state}, \Lambda', S, \Sigma \rangle
\end{equation}
(47)
Note that sometimes \(q_s\) is denoted as \(q_{ts}\), see for example, eq (2.3.76a) of Hirota. We follow the convention of Brown and Carrington and preserve the variable \(q_1\) for the nuclear electric quadrupole coupling constant between different electronic states arising from \(T_2^+(VE)\) which will be the subject of future work. Finally, the diagonal matrix elements of nuclear electric quadrupole coupling are
\begin{align*}
&\langle\text{state}, \nu, \Lambda, S, J, \Omega, I, \rho | H_{\text{q}q_{\text{q}}} | \text{state}, \nu', \Lambda', S', J', \Omega', I, F \rangle \\
&= (-1)^{J' + s + p} \left[ \begin{array}{cc} 1 & F \\ J' & 1 \end{array} \right] \left[ \begin{array}{cc} 1 & 2 \\ F & 1 \end{array} \right]^{-1} \\
&\times (-1)^{J - p} \left[ \begin{array}{cc} 2 & J' \\ 0 & \Omega \end{array} \right]^{2j(2J' + 1)} \delta_{L_\Lambda L_\Lambda'} \\
&\times \frac{1}{4}\langle\text{state}, \nu | q_{\text{q}}(R) | \text{state}, \nu' \rangle
\end{align*}
(48)
while the off-diagonal ones are
\begin{align*}
&\langle\text{state}, \nu, \Lambda, S, J, \Omega, I, \rho | H_{\text{q}q_{\text{q}}} | \text{state}, \nu', \Lambda', S', J', \Omega', I, F \rangle \\
&= (-1)^{J' + s + p} \left[ \begin{array}{cc} 1 & F \\ J' & 1 \end{array} \right] \left[ \begin{array}{cc} 1 & 2 \\ F & 1 \end{array} \right]^{-1} \\
&\times (-1)^{J - p} \left[ \begin{array}{cc} 2 & J' \\ 0 & \Omega \end{array} \right]^{2j(2J' + 1)} \delta_{L_\Lambda L_\Lambda'} \\
&\times \frac{1}{4\sqrt{6}}\langle\text{state}, \nu | q_{\text{q}}(R) | \text{state}, \nu' \rangle
\end{align*}
(49)
As we only consider the hyperfine interactions within a particular electronic state in this paper, the off-diagonal matrix elements arising from \(d(R)\) in eq 41 and \(q_s(R)\) in eq 47 only contribute to the \(\Lambda\)-doubling terms of \(\Omega\) states. In the electron spin resonance spectroscopy literature, the Fermi-contact and nuclear spin–electron spin dipole–dipole terms are, respectively, the first-order isotropic and dipolar contributions to the hyperfine coupling A-tensor. When the second-order contributions of paramagnetic spin orbit (PSO) interaction are considered, the hyperfine coupling constants defined in this paper can be further revised by the PSO terms and determined by the matrix elements of the total hyperfine A-tensor.

4.2 Parity Conserved Matrix Elements under the Rovibronic Wave Functions. Recall the short notation of Hund’s case (\(a_p\)) basis in eq 10, lk, J, I, F) and the basis functions we defined in eq 12, \(|\phi_{mF}^{\text{r}}\rangle, I, F\); the hyperfine matrix elements under the basis set can be expanded as
\begin{align*}
&\langle\phi_{mF}^{\text{r}}, I, F | H_{\text{hf}} | \phi_{m'F'}^{\text{r}}, I, F \rangle \\
&= \langle\phi_{mF}^{\text{r}}, I, F | \sum_{k,l} h_{k,l} | k, J, I, F \rangle (k, J, I, F) \langle k, J, I, F | \phi_{m'F'}^{\text{r}}, I, F \rangle
\end{align*}
(50)
We can rewrite the basis transformation into the matrix format:
\begin{equation}
H_{\text{hf}}^{\text{r}} = (\Phi^{\text{r}})^T H_{\text{hf}}^{\text{r}} \Phi^{\text{r}}
\end{equation}
(51)
\begin{align*}
&\langle\phi_{mF}^{\text{r}}, I, F | H_{\text{hf}} | \phi_{m'F'}^{\text{r}}, I, F \rangle (k, J, I, F) \langle k, J, I, F | \phi_{m'F'}^{\text{r}}, I, F \rangle
\end{align*}
(52)
where \(H_{\text{hf}}^{\text{r}}\) is the matrix of \(H_{\text{hf}}^{(0)}\) (see eq 14 for the matrix elements). Diagonalizing the parity-conserved matrix of each \(F\) results in the energies and wave functions of the hyperfine structure:
\begin{equation}
E_{F}^{\text{r}} = (U_{F}^{\text{r}})^T H_{\text{hf}}^{\text{r}} U_{F}^{\text{r}}
\end{equation}
(53)
The eigenfunction matrix \(U_{F}^{\text{r}}\) is represented in the parity-conserved rovibronic basis set defined in eq 12, which is, however, not very useful for quantum number assignments and wave function analysis. For these purposes, the wave functions can be transformed back in the representation of Hund’s case (a) basis set and the final wave function matrix is
\begin{equation}
\Psi_{\text{F}}^{\text{r}} = \Phi_{\text{F}}^{\text{r}} U_{\text{F}}^{\text{r}}
\end{equation}
(54)
Here, we denote the countable rovibronic wave functions considering nuclear hyperfine interaction as
\begin{equation}
|\psi_{mF}^{\text{r}}\rangle
\end{equation}
(55)
such that
\begin{equation}
\langle\psi_{mF}^{\text{r}}, I, F | H_{\text{hf}} | \psi_{mF}^{\text{r}}, I, F \rangle = \delta_{m,m} E_{mF}^{\text{r}}
\end{equation}
(56)
where \(E_{mF}^{\text{r}}\) is the corresponding eigenvalue of \(|\psi_{mF}^{\text{r}}\rangle\).

The basis transformation procedures from eq 50 to eq 54 reveal the key feature of our variational method which involves accounting for the contribution of every basis function to the final eigenstates. Finally, only \(F, \tau,\) and counting number \(m\) are good quantum numbers.
5. LINE STRENGTH OF THE HYPERFINE TRANSITIONS

In the absence of an external field, the line strength of a nuclear spin resolved rovibronic transition is defined by

\[ S(m, \tau, F \leftrightarrow m', \tau', F') = \sum_{p, M_p} l(m, \tau, F)M_p|T^r_{\tau}(\mu)p(m', \tau', F')|^2 \]

\[ = |\langle \mu \tau | T^r(\mu) | \mu \tau' \rangle|^2 \sum_{p, M_p} \left( \begin{array}{c} F \ 1 \ F' \\ -M_p \ p \ M_p \end{array} \right) \]

\[ = |\langle \mu \tau | T^r(\mu) | \mu \tau' \rangle|^2 \]  

(57)

We initially evaluate the reduced matrix elements of the electric dipole moment by matrix multiplication:

\[ r^F D^r,F = \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \]  

(58)

where \( F D^r \) and \( r^F D^r,F \) are the reduced transition dipole moment matrices in the representation of eq 9 and eq 55, respectively. The following equations give the elements of \( iD^F \), that is, \( \langle k, j, I, F|T^r(\mu)\rangle \), \( k, j, I, F \).

As \( F = J + 1 \) and \( I(T) \) commutes with \( I \),

\[ \langle \text{state}, \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \rangle \]

\[ = \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \]  

\[ = \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \]  

(59)

Rotating the spherical tensor to the body-fixed frame gives

\[ \langle \text{state}, \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \rangle \]

\[ = \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \]  

\[ = \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \]  

(60)

The matrix element \( \langle \text{state}, \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \rangle \) is the same as the one used for the calculation of rovibronic transition intensities excluding nuclear spin in DUO.

\[ \langle \text{state}, \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \rangle \]

\[ = \langle \mu \tau,F'| | F D^r | \mu \tau,F \rangle \]  

(61)

where \( \mu \tau,\mu \tau' \) is the electric dipole moment represented in the body-fixed frame which can be obtained from \textit{ab initio} calculation.

For dipole moment transitions, parity has to be changed and thus follows the selection rule:

\[ \tau: + \leftrightarrow - \]  

(62)

The selection rules on \( F \) comes from the Wigner-6j symbol of eq 59:

\[ \Delta F = -1, 0, 1; \quad \text{and} \quad F \neq 0 \quad \text{if} \quad \Delta F = 0 \]  

(63)

The hyperfine Hamiltonian mixes wave functions with different \( J_i \) as a result, electric dipole transition “forbidden” lines with \( |\Delta J| > 1 \) are observable. For example, when \( I = 1/2 \), we can observe electric dipole transitions of \( O \) and \( S \) branches (\( \Delta J = \pm 2 \)), even if they might be much weaker than the transitions of \( P \), \( Q \), and \( R \) branches.

6. NUMERICAL VERIFICATION

To illustrate and validate our new hyperfine modules, we calculate hyperfine-resolved rotational spectra for electronic and vibrational ground state of \(^{14}\text{N}^{16}\text{O} \) and \(^{24}\text{Mg}^{2}\text{H} \). While both \(^{16}\text{O} \) and \(^{24}\text{Mg} \) have nuclear spin zero; \(^{14}\text{N} \) has \( I = 1 \) and \(^{1}\text{H} \) has \( I = 1/2 \) which allows us to test different coupling mechanisms. For this purpose we compare the results of our DUO calculations with that of PGOPHER using the same model for each calculation. PGOPHER obtains the energy levels and spectra from effective Hamiltonians given appropriate spectral constants. In contrast, DUO takes in coupling curves and performs variational calculations. To get consistent inputs between the two codes it was necessary to simplify the treatment used by DUO.

For \(^{14}\text{N}^{16}\text{O} \) we approximate the DUO solution by using only one contracted vibrational basis function, that is; \( | \Omega = 2, \Pi, \nu = 0 \rangle \) which ensures that we avoid any hyperfine-induced interaction between different vibrational states. In PGOPHER, we used values for the rotational constant, \( B_0 \), and spin–orbit coupling constant matrix, \( A_0 \), computed using DUO:

\[ B_0 = (X^2 \Pi, \nu = 0| \hbar^2 / 2\mu R^2 | X^2 \Pi, \nu = 0) \]  

(64)

\[ A_0 = 2(X^2 \Pi, \nu = 0|C_{SO}(R)|X^2 \Pi, \nu = 0) \]  

(65)

where \( \mu \) is the reduced mass of \(^{14}\text{N}^{16}\text{O} \) and \( C_{SO}(R) \) is the spin–orbit coupling curve. Note that, for spin–orbit interaction, the coupling curve, \( C_{SO}(R) \), describes the coupling energies, while the constant, \( A_i \), is defined by the splitting energies. Thus, \( A \) is defined by twice the matrix element. The NO \( X^2 \Pi \) potential energy curve used by DUO was taken from Wong et al.\(^{15} \) \( C_{SO}(R) \) was assigned an artificial constant \( C_{SO}(R) = 60 \text{ cm}^{-1} \) and the transition dipole moment curve was set to 1 D. Our adopted values for \( B_0 \) and \( A_0 \) are given in Table 1.

| Table 1. Spectroscopic Constants for \(^{14}\text{N}^{16}\text{O} \) Used in This Paper |
|-----------------|---|
| constants       | values [cm\(^{-1}\)] |
| \( B_0 \)       | 1.696 084 011 913 95 |
| \( A_0 \)       | 120 |

For this analysis, the hyperfine coupling was chosen using artificial curves much greater than experimental values. By including only one hyperfine constant at a time, we test the affects of a particular hyperfine interaction. The results are compared in Table 2. Note that, PGOPHER uses nuclear spin–electron spin constants, \( b \), defined by Frosh and Foley,\(^{16} \) rather than \( b'_p \). They are related by the dipole–dipole constant, \( c \),

\[ b_F = b + \frac{c}{3} \]  

(66)

DUO achieves excellent agreement with PGOPHER for the calculation of both the line positions \( \nu \) and line strengths \( S \).
Table 2. Comparison of $^{14}$N$^{16}$O Line Positions and Line Strengths for Calculated Results from DUO and PGOPHER$^{46}$

| Number | 1      | 2      | 3      | 4      |
|--------|--------|--------|--------|--------|
| upper  | $F'$   | 0.5    | 0.5    | 1.5    | 1.5    |
|        | $r'$   |        |        |        |        |
|        | $J'$   | 1.5    | 1.5    | 1.5    | 1.5    |
| lower  | $F'$   | 0.5    | 0.5    | 0.5    | 0.5    |
|        | $r'$   | +      | +      |        |        |
|        | $J'$   | 0.5    | 0.5    | 0.5    | 0.5    |

The slight differences are due to rounding error. As we did not include $\Lambda$-doubling terms in our calculation the wavenumbers corresponding to $b_{0.5}, a$, and $c_{Q_{0.5}}$, and $c_{J}$ in the first and second columns of the same $F = 0.5$ (or in the third and fourth columns, $F = 1.5$) of Table 2 are the same. Hyperfine interactions only split the transitions of different $F$ in the first and third columns (or in the second and fourth columns). In contrast, the wavenumbers obtained with $c_{Q_{0.5}}$ or $d$ included are different from each other even for the same values of $F$ due to the hyperfine contribution to both $\Lambda$-doubling and hyperfine splitting.

We also tested the code for an $I = \frac{1}{2}$ case by calculating pure rotational transitions within the $\nu = 0$, $X^2\Sigma^+$ state of $^{24}$MgH, again using a unit electric dipole moment curve. This is a rather realistic case, as the input spectral constants to PGOPHER listed in Table 3 were determined by the observed transitions.$^{46}$ As for the input to DUO, the potential energy curve was shifted from an empirically determined one$^{7,46}$ to reproduce the $B_{0}$ constant given in Table 3, that is:

$$B_0 = \sqrt{\frac{\hbar^2}{2\mu R^2}} X^2\Sigma^+, \nu = 0$$

The curves of spin-rotation and hyperfine couplings were defined as

$$\gamma(R) = \gamma_0$$

$$b_{\nu}(R) = b_0 + \frac{\epsilon_0}{3}$$

$$c(R) = \epsilon_0$$

Note that the contribution of $D_0$ is not allowed for when only one contracted basis function is used in DUO. Just like the $B_0$ constant, DUO does not use rotational constants, $D_\nu$, $H_\nu$, etc., either, and introduction of these centrifugal distortion would require manipulation of the potential energy curves which are beyond the scope of this work. Nevertheless, DUO still gives hyperfine splittings which are consistent with PGOPHER, see the comparison in Table 4, because $D_0$ uniformly shifts the hyperfine energy levels within the same $N$ rotational levels, where $N$ is the quantum number corresponding to $N$ which is defined as

Table 3. $X^2\Sigma^+$, $\nu = 0$ Spectral Constants of $^{24}$Mg$^1$H Determined by Ziurys et al.$^{46}$ These Values Were Used as the Input to PGOPHER

| constants   | values [MHz] |
|-------------|--------------|
| $B_0$       | 171976.1782  |
| $D_0$       | 10.6212      |
| $\gamma_0$  | 790.809      |
| $b_0$       | 306.277      |
| $\epsilon_0$| 4.792        |


\[ N = J - S \]  
(71)

Table 4. Comparison of \(^{24}\text{Mg}^1\text{H} \ X \Sigma^+_v, \nu = 0 \) Hyperfine Energies Calculated by DUO and PGOPHER\(^a\)

| no. | \( F \) | \( \tau \) | \( J \) | \( N \) | \( E_{DUO} \) | \( E_{PG} \) | difference |
|-----|--------|--------|-----|-----|----------|----------|-----------|
| 1   | 0      | +      | 0.5 | 0   | -230.9057 | -230.9057 | 0.0000    |
| 2   | 1      | +      | 0.5 | 0   | 76.9686   | 76.9686   | 0.0000    |
| 3   | 1      | -      | 0.5 | 1   | 334317.2196 | 334307.7347 | 42.4849   |
| 4   | 0      | -      | 0.5 | 1   | 334236.9188 | 334194.4339 | 42.4849   |
| 5   | 1      | -      | 1.5 | 1   | 344238.9505 | 344196.4655 | 42.4850   |
| 6   | 2      | -      | 1.5 | 1   | 344424.5699 | 344382.0849 | 42.4850   |

\(^a\)Only one vibrational contracted basis function \( \chi \Sigma^+_v, \nu = 0 \) was used in this case. All energies are given in MHz.

We then allowed for the effect of vibrational coupling in DUO by increasing the contracted vibration bases to five functions, that is, \( \chi \Sigma^+_v, \nu = 0, 1, 2, 3, 4 \). As shown in Table 5, vibrational coupling from higher vibrational states automatically introduces centrifugal distortion to the \( \nu = 0 \) state and improves the accuracy of the calculation, compared with the lower rotational levels in Table 4. We did not use a very accurate model here, and thus for higher rotational levels, we still got obvious energy differences in Table 5, and frequency differences in Table 6. The best way to achieve experimental accuracy is to refine the curves by fitting calculated energies or frequencies to measured ones.

Finally, we list two calculated \( S \) branch (\( \Delta J = 2 \)) transitions in the second and fourth rows of Table 7. These hyperfine-induced transitions are much weaker than the two \( R \) branch (\( \Delta J = 1 \)) transitions in the first and third rows.

7. CONCLUSION

We demonstrate an algorithm for the calculation of the hyperfine structure of diatomic molecules based on a variational treatment of nuclear motion. Nuclear magnetic dipole coupling terms including Fermi-contact, nuclear spin-electron spin dipole–dipole interaction, nuclear spin–orbit,
Table 6. Comparison of $^{24}$Mg$^1$H X $^2\Sigma^+$, $\nu = 0$ Hyperfine Line Positions$^a$

| no. | $N'$ | $J'$ | $F'$ | $N''$ | $J''$ | $F''$ | $\nu_{DUO}$ | $\nu_{PG}$ | $s_{DUO}$ | $s_{PG}$ |
|-----|------|------|------|-------|-------|------|-------------|-------------|-----------|----------|
| 1   | 1    | 0.5  | 1    | 0     | 0.5   | 1    | 342997.363  | 342997.763(050) | 1         | 342930.3(20) |
| 2   | 1    | 0.5  | 2    | 0     | 0.5   | 2    | 343117.335  | 343117.463(050) | 1         | 34305.646(050) |
| 3   | 1    | 0.5  | 2    | 0     | 0.5   | 2    | 343305.510  | 343305.646(050) | 1         | 34305.646(050) |
| 4   | 1    | 1.5  | 0    | 0     | 0.5   | 1    | 344119.367  | 344119.497(050) | 1         | 344127.362(050) |
| 5   | 1    | 1.5  | 2    | 0     | 0.5   | 1    | 344304.986  | 344305.125(050) | 1         | 344305.3(20) |
| 6   | 1    | 1.5  | 2    | 0     | 0.5   | 1    | 344427.241  | 344427.362(050) | 1         | 344427.362(050) |
| 7   | 2    | 1.5  | 2    | 1     | 0.5   | 1    | 687155.213  | 687157.17(17) | 1         | 687157.17(17) |
| 8   | 2    | 1.5  | 2    | 1     | 0.5   | 1    | 687169.251  | 687171.00(17) | 1         | 687171.00(17) |
| 9   | 2    | 2.5  | 3    | 1     | 1.5   | 2    | 687959.193  | 687959.54(19) | 1         | 687959.54(19) |
| 10  | 2    | 2.5  | 3    | 1     | 1.5   | 2    | 687972.501  | 687972.66(17) | 1         | 687972.66(17) |
| 11  | 3    | 2.5  | 3    | 2     | 2.5   | 3    | 1028194.809 | 1028202.5(10) | 1         | 1028202.5(10) |
| 12  | 3    | 2.5  | 2    | 2     | 2.5   | 2    | 1028506.511 | 1028512.10(20) | 1         | 1028512.10(20) |
| 13  | 3    | 3    | 4    | 2     | 2.5   | 3    | 1031102.404 | 1031104.29(21) | 1         | 1031104.29(21) |
| 14  | 3    | 3    | 2    | 2     | 2.5   | 2    | 1031107.936 | 1031109.56(21) | 1         | 1031109.56(21) |
| 15  | 3    | 3    | 3    | 3     | 3.5   | 4    | 1369778.585 | 1369779.0(10) | 1         | 1369779.0(10) |
| 16  | 4    | 3    | 3    | 3     | 3.5   | 4    | 1370087.846 | 1370107.5(10) | 1         | 1370107.5(10) |
| 17  | 4    | 3    | 3    | 3     | 3.5   | 4    | 1372686.180 | 1372700.06(98) | 1         | 1372700.06(98) |
| 18  | 4    | 3    | 3    | 3.5   | 2     | 2    | 1372689.271 | 1372700.06(98) | 1         | 1372700.06(98) |
| 19  | 4    | 4    | 5    | 3     | 3.5   | 4    | 1373479.987 | 1373485.81(55) | 1         | 1373485.81(55) |
| 20  | 4    | 4    | 4    | 3     | 3.5   | 3    | 1373483.034 | 1373485.81(55) | 1         | 1373485.81(55) |
| 21  | 6    | 5.5  | 6    | 5     | 4.5   | 5    | 2054132.512 | 2054170.48(71) | 1         | 2054170.48(71) |
| 22  | 6    | 5.5  | 6    | 5.5   | 4.5   | 4    | 2054133.859 | 2054170.48(71) | 1         | 2054170.48(71) |
| 23  | 6    | 6.5  | 7    | 5     | 5.5   | 6    | 2054928.631 | 2054944.05(82) | 1         | 2054944.05(82) |
| 24  | 6    | 6.5  | 6    | 5.5   | 5.5   | 5    | 2054925.966 | 2054944.05(82) | 1         | 2054944.05(82) |

$^a$Five vibrational contracted basis functions IX $^2\Sigma^+$, $\nu = 0, 1, 2, 3, 4$ were used in this case. All frequencies are given in MHz.

Table 7. Comparison of the Line Positions and Strengths in the R and S Branches of $^{24}$Mg$^1$H X $^2\Sigma^+$, $\nu = 0$ Hyperfine Transitions$^b$

| no. | $F'$ | $J'$ | $F''$ | $J''$ | $\nu_{DUO}$ | $\nu_{PG}$ | $S_{DUO}$ | $S_{PG}$ |
|-----|------|------|-------|-------|-------------|-------------|-----------|----------|
| 1   | 2    | +    | 2.5   | 1     | 1           | 1.5         | 687972.505 | 687973.4766 | 1.7558441 | 1.7558510 |
| 2   | 2    | +    | 2.5   | 1     | 1           | 0.5         | 689094.2323 | 689095.2094 | 0.0053314 | 0.0053315 |
| 3   | 3    | -    | 3.5   | 2     | 2           | 2.5         | 1031107.936 | 1031110.8777 | 2.8371019 | 2.8371270 |
| 4   | 3    | -    | 3.5   | 2     | 2           | 1.5         | 1033046.9552 | 1033049.8969 | 0.0014804 | 0.0014805 |

$^b$Line positions are given in MHz. Five vibrational contracted basis functions IX $^2\Sigma^+$, $\nu = 0, 1, 2, 3, 4$ were used in this case. The line strength, $S_{[Debye]}$, has the same definition as that in PGOPHER when the intensity unit option of PGOPHER, IntensityUnit, is chosen as Noitolondon, and the transition dipole moment is set to 1 D.
to gradually update DUO for each of these cases as the need arises.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.1c01244.

Duo and PGOPHER input files used in this work (PDF)

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Notes
The authors declare no competing financial interest.

Duo is an open-source software, which is available at https://github.com/ExoMol/Duo, where Duo input files used in this work can be found.

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