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Spectroscopic calculation of asymmetric top free radicals: method and program*

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Abstract This paper sketches out the effective Hamiltonian and basis set adopted in the spectroscopic calculation of asymmetric top free radicals, and details the machine implementation of the spectral analysis of asymmetric top free radicals, the design and usage of the program package. To demonstrate the application of this program, analyses have been performed on the far infrared laser magnetic resonance spectrum of $^{14}N^{16}O_2(I = 1)$ and the infrared diode laser spectrum of the ν_3 band of $PO_2(I = 1/2)$ using the program.

Keywords: asymmetric top free radicals, molecular spectroscopy, theoretical calculation.

The spectroscopy of free radical intermediates in chemical reactions has attracted increasing attention during the recent three decades. Amongst the family of free radicals, asymmetric top molecules constitute a large proportion, and many free radicals of special interests, such as PO_2, NO_2, CH_2F, HCO, etc. are of asymmetric rotors.

The disadvantage inherent in the laser magnetic resonance (LMR) technique lies in the difficulty in analyzing the spectra, especially for asymmetric top free radicals. The complication of asymmetric top free radicals in structure and the involvement of Zeeman effect in an external magnetic field give rise to such a difficulty.

Sears has developed a program for detailed analysis of asymmetric top free radicals in his systematic study on the LMR spectroscopy of asymmetric top free radicals[1,2]. Unfortunately, Sears' program could not deal with the high lying transitions or even the low lying transitions of those species subjected to severe centrifugal distortion as it does not include the high order centrifugal distortion corrections in the effective Hamiltonian. The calculation of zero field spectra is not included in that program and its efficiency is also very limited in the search for magnetic resonance lines. This paper is intended to make some improvements to break through the above limitations.

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1 Effective Hamiltonian and basis set

The calculation of complicated spectra is usually implemented numerically using the effective Hamiltonian. The effective Hamiltonian may assume several different forms and here we adopt the most widely accepted one

$$H = H_{\mathrm{W}} + H_{\mathrm{FS}} + H_{\mathrm{HFS}} + H_{\mathrm{Z}}, \tag{1}$$

where H_{w} denotes the Watson's A-reduced Hamiltonian; H_{FS} and H_{HFS} are those taken account of the fine and hyperfine structure energy contributions, respectively; and H_{Z} represents the Zeeman interaction between the molecule and an external magnetic field.

The Watson's A-reduced Hamiltonian is given by[3]

$$H_{\mathrm{W}} = H_{\mathrm{R}} + H_{\mathrm{CD}}, \tag{2}$$

where the rotational operator

$$H_{\mathrm{R}} = AN_{\mathrm{z}}^2 + BN_{\mathrm{x}}^2 + CN_{\mathrm{y}}^2 = \frac{B+C}{2}N^2 + \left(A - \frac{B+C}{2}\right)N_{\mathrm{z}}^2 + \frac{B-C}{2}N_{\mathrm{xy}}^2, \tag{3}$$

and the centrifugal distortion correction to the rotational energy may be written as

$$\begin{aligned} H_{\mathrm{CD}} = & - \Delta_{\mathrm{N}}N^4 - \Delta_{\mathrm{NK}}N^2N_{\mathrm{z}}^2 - \Delta_{\mathrm{K}}N_{\mathrm{z}}^4 - 2\delta_{\mathrm{N}}N^2N_{\mathrm{xy}}^2 - \delta_{\mathrm{K}}\{N_{\mathrm{z}}^2, N_{\mathrm{xy}}^2\} \\ & + H_{\mathrm{N}}N^6 + H_{\mathrm{NK}}N^4N_{\mathrm{z}}^2 + H_{\mathrm{KN}}N^2N_{\mathrm{z}}^4 + H_{\mathrm{K}}N_{\mathrm{z}}^6 \\ & + 2h_{\mathrm{N}}N^4N_{\mathrm{xy}}^2 + h_{\mathrm{NK}}N^2\{N_{\mathrm{z}}^2, N_{\mathrm{xy}}^2\} + h_{\mathrm{K}}\{N_{\mathrm{z}}^4, N_{\mathrm{xy}}^2\} \\ & + L_{\mathrm{N}}N_{\mathrm{z}}^8 + L_{\mathrm{NNK}}N^6N_{\mathrm{z}}^2 + L_{\mathrm{NK}}N^4N_{\mathrm{z}}^4 + L_{\mathrm{KKN}}N^2N_{\mathrm{z}}^6 + L_{\mathrm{K}}N_{\mathrm{z}}^8 \\ & + 2l_{\mathrm{N}}N^6N_{\mathrm{xy}}^2 + l_{\mathrm{NK}}N^4\{N_{\mathrm{z}}^2, N_{\mathrm{xy}}^2\} + l_{\mathrm{KN}}N^2\{N_{\mathrm{z}}^4, N_{\mathrm{xy}}^2\} + l_{\mathrm{K}}\{N_{\mathrm{z}}^6, N_{\mathrm{xy}}^2\} \\ & + P_{\mathrm{N}}N^{10} + P_{\mathrm{NNK}}N^8N_{\mathrm{z}}^2 + P_{\mathrm{NK}}N^6N_{\mathrm{z}}^4 + P_{\mathrm{KN}}N^4N_{\mathrm{z}}^6 + P_{\mathrm{KKN}}N^2N_{\mathrm{z}}^8 + P_{\mathrm{K}}N_{\mathrm{z}}^{10} \\ & + 2p_{\mathrm{N}}N^8N_{\mathrm{xy}}^2 + p_{\mathrm{NNK}}N^6\{N_{\mathrm{z}}^2, N_{\mathrm{xy}}^2\} + p_{\mathrm{KKN}}N^2\{N_{\mathrm{z}}^6, N_{\mathrm{xy}}^2\} + p_K\{N_{\mathrm{z}}^8, N_{\mathrm{xy}}^2\} \\ & + Q_{\mathrm{NNK}}N^8N_{\mathrm{z}}^4 + Q_{\mathrm{KKN}}N^4N_{\mathrm{z}}^8 + Q_{\mathrm{KKKN}}N^2N_{\mathrm{z}}^{10} + Q_KN_{\mathrm{z}}^{12}, \end{aligned} \tag{4}$$

In Eqs. (3) and (4), $N_{\mathrm{xy}}^2 = N_{\mathrm{x}}^2 - N_{\mathrm{y}}^2$; $\{A, B\} = AB + BA$.

The centrifugal distortion correction to the spin-rotation interaction in H_{FS}, the fine structure Hamiltonian, may be expressed as

$$H_{\mathrm{SRCD}} = \Delta_{\mathrm{N}}^{\mathrm{S}}N^2(N \cdot S) + \frac{1}{2}\Delta_{\mathrm{NK}}^{\mathrm{S}}\{N^2, N_{\mathrm{z}}S_{\mathrm{z}}\} + \Delta_{\mathrm{KN}}^{\mathrm{S}}N_{\mathrm{z}}^2 N \cdot S + \Delta_{\mathrm{K}}^{\mathrm{S}}N_{\mathrm{z}}^3S_{\mathrm{z}}$$

$$+ \delta_{\mathrm{N}}^{\mathrm{S}} \mathrm{N}_{\mathrm{xy}}^{2} N \cdot S + \frac{1}{2} \delta_{\mathrm{K}}^{\mathrm{S}} \{ N_{\mathrm{xy}}^{2}, \; N_{\mathrm{z}} S_{\mathrm{z}} \} + H_{\mathrm{K}}^{\mathrm{S}} \mathrm{N}_{\mathrm{z}}^{5} S_{\mathrm{z}} + L_{\mathrm{K}}^{\mathrm{S}} \mathrm{N}_{\mathrm{z}}^{7} S_{\mathrm{z}}. \quad (5)$$

Compared with Ref. [1], the centrifugal distortion correction to the rotational energy is extended up to the twelfth terms in Eq. (4) and the centrifugal distortion correction to the spin-rotation interaction up to the eighth term in Eq. (5). It will be proved that the high order centrifugal distortion terms have conspicuous effects on the energy levels especially those high-lying rotational levels.

For asymmetric top molecules, we expect the spin-orbit coupling to be very small and the spin-rotation coupling to be relatively strong hence Hund's case (b) coupling scheme is appropriate. The fully coupled representation is adopted here

$$\boldsymbol{N} + \boldsymbol{S} = \boldsymbol{J}, \; \boldsymbol{J} + \boldsymbol{I} = \boldsymbol{F}, \quad (6)$$

and the parity conserving basis

$$| \eta N K_a m \pm \rangle = 2^{-1/2} \{ | \eta N K_a m \rangle \pm (-)^{N-K_a} | \eta N - K_a m \rangle \}. \quad (7)$$

The theoretical background of the program is detailed in a separate paper$^{1)}$.

2 Machine implementation

The Hamiltonian matrix can only be built in a particular basis vector space. The energy levels are the eigenvalues of the Hamiltonian matrix. However, the Hilbert space that consists of all basis vectors is of infinite dimensions so the Hamiltonian matrix based on it is also of infinite dimensions. The calculation of energy levels can be implemented by constructing the basis vector sub-space within a designated range of quantum numbers around the level to be calculated and by setting up the Hamiltonian sub-matrix in the sub-space; then via diagonalization of the Hamiltonian sub-matrix the energy level is calculated[1]. Table 1 illustrates the basis vector sub-spaces for calculating the six $6_{1,5}$ hyperfine structure levels of NO_2 X^2A_1, where the basis vector sub-spaces are truncated at $\Delta N = \pm 1$ and $\Delta K = \pm 4$ around the levels to be calculated.

The Hamiltonian sub-matrix can be constructed by calculating all its elements in the basis vector sub-space corresponding to the calculated level. The energy of the calculated level can be obtained by diagonalizing the Hamiltonian sub-matrix. The diagonalization is accomplished by a library routine that uses a Householder transformation to change the matrix into tridiagonal form followed by the QL algorithm which completes the process. The eigenvalues are sorted in ascending order and appropriate adjustment is made to the eigenvector array $\boldsymbol{S}$ to keep the corresponding relations between the eigenvalues and the eigenvectors unchanged. More details about the principle and the library routine of matrix diagonalization can be found in Ref. [4]. The transition frequencies can be obtained in terms of the selection rules for asymmetric top molecules after the calculation of energy levels.

In the analysis of LMR spectra, it is necessary to divide the scanning range of a magnetic field into several equal intervals and then to calculate the energy levels and transition frequencies at differ-

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1) Liu, Y. et al. Spectroscopic analysis of asymmetric top free radicals. accepted by Science in China, Ser. B.

Table 1 Basis vector sub-spaces for calculating the six $6_{1,5}$ hyperfine structure levels of NO_2 X^2A_1 a)b)

$J=5.5$, $F=4.5$			$J=5.5$, $F=5.5$ $J=6.5$, $F=5.5$			$J=5.5$, $F=6.5$ $J=6.5$, $F=6.5$			$J=6.5$, $F=7.5$		
N	K	J	N	K	J	N	K	J	N	K	J
5	1	4.5	5	1	4.5	5	1	5.5	6	1	6.5
5	3	4.5	5	3	4.5	5	3	5.5	6	3	6.5
5	5	4.5	5	5	4.5	5	5	5.5	6	5	6.5
5	1	5.5	5	1	5.5	6	1	5.5	7	1	6.5
5	3	5.5	5	3	5.5	6	3	5.5	7	3	6.5
5	5	5.5	5	5	5.5	6	5	5.5	7	5	6.5
6	1	5.5	6	1	5.5	6	1	6.5	7	1	7.5
6	3	5.5	6	3	5.5	6	3	6.5	7	3	7.5
6	5	5.5	6	5	5.5	6	5	6.5	7	5	7.5
			6	1	6.5	7	1	6.5			
			6	3	6.5	7	3	6.5			
			6	5	6.5	7	5	6.5			
			7	1	6.5	7	1	7.5			
			7	3	6.5	7	3	7.5			
			7	5	6.5	7	5	7.5			

a) For $^{14}N^{16}O_2$, the electronic spin is 1/2 and the nuclear spin is 1; b) truncated at $\Delta N = \pm 1$ and $\Delta K = \pm 4$.

ent field positions. If the transition frequency is close to the laser frequency at a certain field position, then the field position, where the magnetic resonance occurs, and the transition frequency is equal to the laser frequency, can be calculated by a three-point interpolation. Obviously, taking a smaller step in the magnetic field would be better if the non-linearity of Zeeman effect becomes remarkable (such a circumstance often occurs at the high field).

Zeeman tuning rate, the rate at which the energy level or transition frequency ν is tuned in the magnetic field B, is usually very useful in the analysis of LMR spectra. The tuning rate for the transition frequency can be obtained by subtracting the tuning rate for the lower level $\frac{\partial E_b}{\partial B}$ from that for the upper level $\frac{\partial E_a}{\partial B}$,

$$\frac{\partial \nu_{ab}}{\partial B} = \frac{\partial E_a}{\partial B} - \frac{\partial E_b}{\partial B}, \tag{8}$$

and the tuning rates for the energy levels can be evaluated by the formula as follows:

$$\frac{\partial E_i}{\partial p_j} = \left[\boldsymbol{S} \cdot \frac{\partial \boldsymbol{H}}{\partial p_j} \cdot \boldsymbol{S}^T \right]_{ii}, \tag{9}$$

where E_i represents the ith eigenvalue of the Hamiltonian sub-matrix, p_j the jth molecular parameter, S the eigenvector matrix, and $\frac{\partial \boldsymbol{H}}{\partial p_j}$ the derivative of the Hamiltonian to the jth parameter[5].

After a successful assignment of quantum numbers to spectral lines, molecular parameters can be improved through the least squares fit of experimental data. This step allows one to extract the knowledge of molecular structure from experimental spectra. Sears[1] introduced a library routine using the singular value decomposition (SVD) algorithm in his least squares fitting program. The success of the SVD algorithm is derived from its good stability and fast convergence. However, the singular values need truncating and editing according to a manually specified criterion; the fitting results, i.e. molecular parameters and their standard deviations, vary substantially with such a criterion (Ref. [4], Chap. 15.4).

By means of the principle and algorithm for the least squares fit in Ref. [6], we have developed a new least squares fitting routine without any artificial work. The input data set for calling this routine includes the calculation errors in the transition frequencies stored in a one-dimensional array $\boldsymbol{Y}(N)$, the weights for data points stored in a one-dimensional array $\boldsymbol{W}(N)$, and the derivatives of transition frequencies to molecular parameters stored in a two-dimensional array $\boldsymbol{D}(n, N)$. Here N denotes the number of data points, and n the number of fitted parameters. For the ith data point, the frequency error y_i is defined as the difference between observed and calculated values, the weight w_i is normally set to the reciprocal of the square of experimental uncertainty, and D_{ij}, the derivative to the jth fitted parameter a_j, can be calculated in terms of Eq. (9). Define arrays α and β as follows:

$$\alpha_{jk} = \sum_{i=1}^{N} w_i D_{ij} D_{ik}, \qquad \beta_k = \sum_{i=1}^{N} w_i y_i D_{ik}. \tag{10}$$

The adjustments to fitted parameters are determined by the following equations:

$$\beta_k = \sum_{j=1}^{n} \delta a_j \alpha_{jk}, \tag{11}$$

where δa_j represents the adjustment to the parameter a_j. The above equations can be written in a matrix form

$$\beta = \delta \boldsymbol{a} \alpha. \tag{12}$$

The error matrix ε is the inverse of the array α,

$$\varepsilon = \alpha^{-1}. \tag{13}$$

The adjustment to the parameter a_j and the standard deviation can be derived from the error matrix ε,

$$\delta a_j = \sum_{k=1}^{N} \beta_k \varepsilon_{jk}, \quad \sigma a_j = \varepsilon_{jj}^{1/2}. \tag{14}$$

Molecular constants can be optimized by adjusting their values according to the calculated adjustment to minimize the value of the merit function $\chi^2 = \sum_{i=1}^{N} w_i y_i^2$.

3 Profile of program

The program package for the detailed analysis of spectra of asymmetric top free radicals consists of four mutually constructive and interactive parts.

Part 1 is the prediction program of the zero field spectrum. There is no equivalent part in Sears' program. By constructing basis vector sub-space, setting up Hamiltonian sub-matrix, and diagonalizing the Hamiltonian sub-matrix, energy levels can be obtained. According to the selection rule, the frequencies for all possible transitions can be calculated. With the main molecular constants and the search range for rotational quantum number N as the input, the zero field spectrum prediction program will yield all zero field energy levels and frequencies for all possible transitions within the rotational quantum number range. This program greatly helps spectroscopic experimentation since the search area could be narrowed according to the zero field spectrum prediction. Moreover, the zero field spectrum prediction is extremely useful for the assignment of the zero field or LMR spectra. Accurate zero field spectrum prediction may relieve some blind search in the process of the test trial assignment to LMR spectra.

Part 2 is the prediction program of LMR spectrum. This program searches magnetic resonance lines in a full range. Firstly, expand each zero field transition whose frequency is close to the laser frequency, calculate each Zeeman component with magnetic quantum number satisfying $|M_F| \leqslant F$, and search for all field positions at which magnetic resonance may occur. And then calculate the transition frequency at each possible field position, the difference between the transition frequency and the laser frequency, the relative intensity and Zeeman tuning rate. Relatively precise molecular constants and quantum numbers for those zero field transitions whose frequencies are close to the laser frequency derived from the zero field spectrum prediction are needed in the input data set for this calculation. Tentative assignment to spectral lines can be made in terms of predicted field positions, relative intensities and Zeeman tuning rates. Magnetic quantum numbers are needed in the input data set in Sears' program. This does limit its power in the search for magnetic resonance lines. Our program improves much with respect to the above point.

Part 3 is the magnetic resonance assignment program, which makes assignments on the basis of the results on the tentative assignment in Part 2. The field positions at which transition frequencies are calculated are their observed values in this part instead of the calculated values as in the LMR spectrum prediction. One can make sure whether the tentative assignment is successful or not by comparing the observed and calculated values in the transition frequency and referring to the relative intensities of spectral lines and Zeeman tuning rates. The results of the tentative assignments are needed in the input data set for this calculation.

Part 4 is the molecular constant fitting program, which is the final goal of the spectroscopic calculation. The initial values for molecular constants, quantum numbers for the upper and lower levels derived from the zero field or LMR spectrum prediction, observed values for transition frequencies and field positions, and experimental uncertainties are needed in the input data set for this calculation. The criterion for terminating the execution of least squares fitting program should also be specified. In this part, molecular constants are refined by least squares fitting program. And the transition frequencies, relative intensities, field positions, and Zeeman tuning rates of all lines are calculated repeatedly using the optimized molecular constants.

4 Applications

One can understand the molecular structure only after making assignments to spectral lines, because unassigned spectral lines have little significance. Employing the program described above, we have made an assignment to the far infrared (FIR) LMR spectrum of $^{14}N^{16}O_2$ and performed a global fit on the ν_3 band of the PO_2 radical.

In Table 2 is given the assignment to the FIR LMR spectrum of $^{14}N^{16}O_2$ in its ground vibrational state observed at 964 313.4 MHz. The assignment to magnetic resonance transitions of $6_{3,3} \leftarrow 7_{2,6}$ and $5_{3,3} \leftarrow 6_{2,4}$ made in this work is just the same as that given by Curl et al. and Brown et al.[7,8]. The high lying rotational magnetic resonance transitions of $39_{2,38} \leftarrow 39_{1,39}$ are demasked for the first time. These observed lines have escaped from the assignments made by Curl et al. and Brown et al. since they did not include the high order centrifugal distortion contributions in the Hamiltonian; however, the high order centrifugal distortion contributions to the high lying rotational levels of $^{14}N^{16}O_2$ proved to be non-negligible[9].

Table 2 Assignment to the FIR LMR spectrum of $^{14}N^{16}O_2$ in the ground vibrational state observed at 964313.4 MHz

N'	K'_a	K'_c	M'_F	$P' \leftarrow$	N''	K''_a	K''_c	M''_F	P''	Field/G	(O-C)/G	$(\partial v/\partial B)$ /MHz·G^{-1}
6	3	3	2.5	-1	7	2	6	3.5	1	2 746.2	0.06	2.56
6	3	3	-4.5	-1	7	2	6	-5.5	1	4 604.0	-1.09	2.59
5	3	3	-1.5	-1	6	2	4	-2.5	1	5 394.4	0.96	-2.57
5	3	3	-4.5	-1	6	2	4	-5.5	1	6 651.8	0.47	-2.70
39	2	38	-38.5	1	39	1	39	-38.5	-1	10 184.2	0.06	2.28
39	2	38	-35.5	1	39	1	39	-36.5	-1	10 261.1	0.41	2.30
39	2	38	-31.5	1	39	1	39	-31.5	-1	10 481.1	-0.24	2.38
39	2	38	-25.5	1	39	1	39	-26.5	-1	10 645.9	-0.67	2.44
39	2	38	-19.5	1	39	1	39	-19.5	-1	10 838.7	-0.19	2.51
39	2	38	-9.5	1	39	1	39	-10.5	-1	11 114.4	0.03	2.59
39	2	38	-6.5	1	39	1	39	-7.5	-1	11 199.8	0.04	2.62
39	2	38	14.5	1	39	1	39	15.5	-1	11 722.3	0.25	2.74

As another example in the application of our program, we have also carried out a global analysis of the ν_3 band of the PO_2 radical. The global analysis turns out to be a new set of molecular constants for the ν_3 band of the PO_2 radical, which has been the most precise hitherto. The newly improved parameters and the results given in Ref. [10] are listed in Table 3. As shown by the table, the overall precision for molecular constants in this work is higher than that given in Ref. [10] by about one order of magnitude.

Table 3 Molecular constants for the ν_3 band of the PO_2 radical in the ground electronic state

Constant/cm^{-1}		Ref. [10]	Present work
	v_0	1 327.534 52(69)$^{a)}$	1 327.534 96(12)
	A	3.408 323(69)	3.408 322 7(27)
	B	0.285 913 0(43)	0.285 912 25(42)
	C	0.263 061 6(43)	0.263 061 28(42)
10^3	Δ_K	0.907 7(33)	0.907 681(58)
10^4	Δ_{NK}	-0.129 54(56)	-0.129 539(77)
10^6	Δ_N	0.158 8(13)	0.158 92(14)
10^5	δ_K	0.166(57)	0.159(15)
10^7	δ_N	0.339 1(96)	0.339 2(19)
10^6	H_K	0.831(56)	0.827 8(22)
10^8	H_{KN}	-0.903(82)	-0.900(36)
10^9	H_{NK}	-0.183	-0.186(18)
10^{11}	H_N	-0.343	-0.331(22)
10^9	h_{KN}	-0.20	-0.20
10^{12}	h_N	0.31	0.31
10^8	L_K	-0.103(29)	-0.106 9(24)
10	ϵ_{aa}	0.531 7(14)	0.532 24(52)
10^3	ϵ_{bb}	0.713(93)	0.708(40)
10^2	ϵ_{cc}	-0.148 4(93)	-0.151 6(40)

a) One standard deviation in parenthesis, in units of least significant digit.

5 Discussion

The program package for detailed analysis of spectra of asymmetric top free radicals described in this paper is based on Sears' program. The present work (i) improves the theoretical model by introducing the high order centrifugal distortion terms to the effective Hamiltonian, which is of great significance for calculating high lying rotational transitions; (ii) develops a zero field spectrum prediction program, which relieves the spectroscopic experimentation from some blind search and greatly helps assign spectral lines; (iii) enlarges the search range to the full coverage in the LMR spectrum prediction to minimize artificial efforts hence promoting the efficiency in analysis; (iv) develops a new least squares fitting program in order to eliminate any effects of artificial work on fitting results.

In order to test our program package and illustrate its usage, we have applied it to analyzing the FIR LMR spectrum of $^{14}N^{16}O_2$ and the ν_3 band of the PO_2 radical. The high lying rotational magnetic resonance transitions of $^{14}N^{16}O_2$ have been assigned for the first time. The most precise molecular constants for the ν_3 band of the PO_2 radical have also been obtained. It is proved that this efficient program package can be used for detailed analysis of spectra of asymmetric top free radicals and has a bright future. Obviously, the package may also be used for analysis of spectra of other asymmetric top molecules which are not free radicals although it is designed for free radicals.

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