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Optimal generalized internal vibrational coordinates and potential energy surface for the ground electronic state of SO₂

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An optimization of generalized internal vibrational coordinates for the electronic ground state of the SO₂ molecule is carried out. These coordinates are given by the magnitudes and the angle formed by two vectors expressed as linear combinations of the internal valence vectors, and depend on two external parameters which can be optimized so as to reduce the vibrational coupling of the molecule as much as possible. The optimal values of the parameters are found by minimizing a set of unconverged vibrational energies which are computed variationally using a small basis function set. It is shown that the optimal internal coordinates obtained for SO₂ are superior to both valence and Radau coordinates, as well as to a set of normal coordinates previously derived by proper rotation of the Jacobi S–O₂ coordinates. These optimal internal coordinates are then applied to calculate the vibrational energies of the molecule using an *ab initio* force field expressed as a Morse-cosine expansion, and then to refine it by nonlinear least-squares fitting to the observed vibrational frequencies. © 2001 American Institute of Physics. [DOI: 10.1063/1.1377893]

I. INTRODUCTION

The ground electronic state, \tilde{X}^1A_1 , of the SO₂ molecule has been extensively studied throughout the years, both theoretically^{1–21} and experimentally.^{22–32} Various potential energy surfaces have been determined for this state, including empirical fits as those performed by Kuchitsu and Morino,¹ Farantos *et al.*,³ Carter *et al.*,⁵ and Kauppi and Halonen,¹¹ and also the *ab initio* calculations carried out by Pack and Woods,¹⁴ and by Martin¹⁶ at the coupled cluster [CCSD(T)] level. Some of these surfaces have been used to investigate both the stochasticity of the vibrational spectrum and the transition from normal to local modes, by means of classical trajectories.^{4,7,20} Guo and co-workers^{17,18} have recently considered these issues from a quantum perspective by performing extensive variational calculations of highly excited vibrational states up to 25 000 cm^{–1}.^{17,18} Sibert *et al.*^{9,10,13} have studied the vibrational states of SO₂ and their rotation–vibration mixing by using canonical Van Vleck perturbation theory.

The experimental observations of the vibrational–rotational frequencies of the SO₂ ground electronic state essentially go back to the original infrared spectrum recorded by Shelton *et al.*²² almost fifty years ago, and flow into the more recent high resolution measurements made by Guelachvili²⁵ and Flaud *et al.*^{28–32} on a number of rovibrational bands using Fourier transform spectroscopy. The dispersed fluorescence (DF) emission from the \hat{C}^1B_2 electronic state has also been of much use in observing SO₂ vibrational energy levels of the ground state. Brand *et al.*²³ measured the DF spectrum excited by the 210 nm line of Zn⁺, and extracted from it a total of 37 vibrational terms below 7000 cm^{–1}. More recently, Yamanouchi and co-workers^{26,27} have

identified a large number of highly excited vibrational levels distributed between 17 300 and 22 500 cm^{–1} from the DF and stimulated emission pumping (SEP) spectra, and have assigned many of them by using a Dunham-type expansion. Sako and Yamanouchi¹⁵ have also fitted these levels to an algebraic Hamiltonian expansion which makes it possible to construct the vibrational wavefunctions and therefore to use them to study the normal-to-local mode transition.

Use of good coordinate systems is essential for properly describing and understanding better the vibrational motions of polyatomic molecules, especially for excited states in which the vibrational couplings and anharmonicities become of non-negligible magnitude.^{13,33–38} Besides standard rectilinear normal coordinates,^{2,5} other curvilinear systems such as valence^{8,11,12} and Radau^{17,18} coordinates have been used to determine vibrational energy levels and wavefunctions of the SO₂ electronic ground state. Radau and valence coordinates are particular cases of the so-called generalized internal coordinates,^{35,39–42} which are defined as linear coordinates of the internal valence vectors of the molecule; they can therefore be properly optimized in order to reduce the vibrational couplings and thus achieve a faster convergence in variational calculations. Different applications of internal generalized coordinates have been successfully carried out in our group to the linear triatomic molecules of CO₂,^{42,43} CS₂,⁴⁴ N₂O,⁴¹ and OCS.⁴⁵

The central objective of this work is to find a system of optimal generalized internal coordinates for the electronic ground state of the SO₂ molecule. To accomplish this, we analyze the variations of a set of vibrational energy levels of the molecule calculated variationally using a reduced set of basis functions, with respect to the external parameters which characterize the generalized internal coordinates. The potential energy surface for SO₂ employed to perform the

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coordinates optimization is the empirical potential determined by Kauppi and Halonen.¹¹ This potential function is expressed as a fourth order series expansion in terms of the Morse variable for the valence radial coordinates and the polynomial displacement variable for the angular coordinate. Once the optimal internal coordinates for SO₂ are obtained, they are used to carry out a new empirical adjustment of the potential energy surface of the molecule by using a Morse-cosine expansion to represent the surface and taking an accurate *ab initio* force field, recently determined by Martin,¹⁶ as the starting point in the fit. The paper is organized as follows: in Sec. II after a brief sketch of the generalized internal coordinates, the variational optimization of their external parameters for the SO₂ molecule is presented; Sec. III contains the details of the fitting of the potential energy surface and finally in Sec. IV the conclusions extracted from this study are given.

II. OPTIMIZATION OF COORDINATES

The generalized internal vectors for a triatomic molecule, \mathbf{t}_1 and \mathbf{t}_2 , are defined as linear combinations of the internal valence vectors, \mathbf{R}_1 and \mathbf{R}_2 , as follows:^{35,39,40–42}

$$\mathbf{t}_1 = \frac{1}{(1-ab)^{1/2}}(\mathbf{R}_1 + a\mathbf{R}_2), \quad (1)$$

$$\mathbf{t}_2 = \frac{1}{(1-ab)^{1/2}}(b\mathbf{R}_1 + \mathbf{R}_2), \quad (2)$$

where the parameters a and b specify the orientation of the generalized internal vectors and where the scale factor $1/(1-ab)^{1/2}$ guarantees that the Jacobian of the transformation is equal to unity. The generalized internal vibrational coordinates are the magnitudes t_1 and t_2 of the internal vectors and the angle, θ , that they form. The pure vibrational Hamiltonian ($\mathbf{J}=0$) for these coordinates can be written as follows:^{39,40}

$$\begin{aligned} \hat{H}_{\text{vib}} = & -\frac{\hbar^2}{2} \left[\frac{1}{\mu_{11}} \frac{\partial^2}{\partial t_1^2} + \frac{1}{\mu_{22}} \frac{\partial^2}{\partial t_2^2} + \left(\frac{1}{\mu_{11}t_1^2} + \frac{1}{\mu_{22}t_2^2} - \frac{2 \cos \theta}{\mu_{12}t_1t_2} \right) \right. \\ & \times \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \left. \right] + \frac{\hbar^2}{\mu_{12}} \left[-\cos \theta \frac{\partial^2}{\partial t_1 \partial t_2} \right. \\ & + \left(\frac{1}{t_1 \partial t_2} + \frac{1}{t_2 \partial t_1} - \frac{1}{t_1 t_2} \right) \left(\sin \theta \frac{\partial}{\partial \theta} + \cos \theta \right) \left. \right] \\ & + \hat{V}(t_1, t_2, \theta), \end{aligned} \quad (3)$$

where the volume element is $d\tau = \sin \theta dt_1 dt_2 d\theta$, and where the reduced masses μ_{11} , μ_{22} , and μ_{12} depend on the external parameters a and b .⁴⁵ It is convenient to redefine the external parameters in the angular form⁴¹

$$\alpha = \arctan a, \quad (4)$$

$$\beta = \arctan b. \quad (5)$$

Coordinates (t_1, t_2, θ) contain, as particular cases, the sets of valence, center of mass, and orthogonal Jacobi and Radau coordinates.^{41,45} The analytical expressions which give the

TABLE I. Values of the external parameters (α, β) for different internal coordinate systems of the SO₂ molecule.

Coordinate system	α	β
Valence	0.0°	0.0°
Center of mass	−18.4°	−18.4°
Jacobi S–OO'	−45.0°	45.0°
Radau O–SO'	−31.0°	18.4°
Jacobi O–SO'	−18.4°	0.0°
Radau S–OO'	−9.8°	−9.8°
Jacobi O'–SO	0.0°	−18.4°
Radau O–SO'	18.4°	−31.0°

external parameters α and β in terms of the atomic masses for these coordinate systems can be found in Ref. 45. In Table I we include the corresponding values of the external parameters for the SO₂ molecule. These values can also be represented⁴¹ in a rhombus-shape plane which includes all the (α, β) values which give different generalized internal coordinate systems. Such a representation for SO₂ is shown in Fig. 1.

As in our previous work,^{41,42,44,45} we determine the optimal generalized internal vibrational coordinates for SO₂ by carrying out variational calculations of the vibrational energies of the molecule with reduced sets of basis functions, and by analyzing the variations of the unconverged energies as a function of the optimization parameters. Concretely, we use a set of 60 basis functions constructed as products of the anharmonic wavefunctions obtained from one-dimensional cuts of the Hamiltonian at the equilibrium point. The three-dimensional basis functions are selected as those which provide the lowest diagonal elements of the Hamiltonian matrix. To solve the anharmonic eigenvalue equations we use the DVR method,^{46,47} with DVR basis functions based on harmonic oscillators for the radial coordinates t_1 and t_2 and on Jacobi polynomials for the angular coordinate θ .^{48,49} The parameters that characterize the primitive DVR harmonic and Jacobi functions are chosen so as to fit the harmonic force constants of the potentials in generalized internal coor-

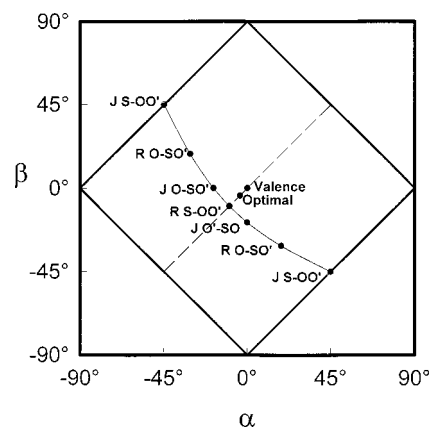


FIG. 1. The location of different coordinate systems for the SO₂ molecule in the (α, β) plane. R and J stand for Radau and Jacobi, respectively. The solid line corresponds to the orthogonal coordinate systems and the dashed line to the symmetrical ($\alpha = \beta$) coordinate systems.

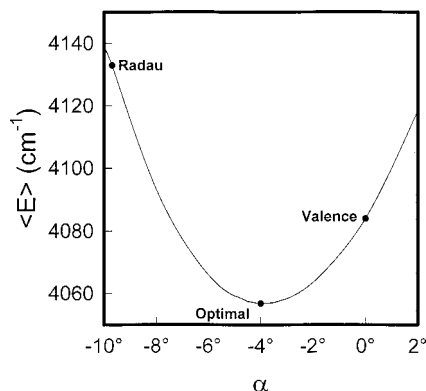


FIG. 2. The average value of the unconverged vibrational energies of SO_2 computed using generalized internal coordinates.

ordinates. The potential energy function used in these calculations is the full variational (FV) Morse potential expansion determined empirically by Kauppi and Halonen¹¹ (KH).

The search for optimal generalized internal coordinates of the SO_2 molecule is performed by inspecting the variations of the unconverged vibrational energies of a set of low-lying states of the molecule, with respect to the angular external parameters α and β . The vibrational states of SO_2 can be properly gathered in blocks labeled by the polyad quantum number $N = v_1 + v_3 + v_2/2$,¹¹ where v_1 and v_3 are the normal mode quantum numbers for the symmetric and antisymmetric stretches, respectively, and v_2 is the normal quantum number for the bend. We study the variations of the energies for the states belonging to the blocks $N=0$ to $N=3$, which gives a total of 30 vibrational states.

The symmetry of the SO_2 molecule suggests that symmetrical generalized internal coordinates, i.e., those for which $\alpha = \beta$, are to be preferred as optimal, and this is effectively confirmed by preliminary optimization calculations. Accordingly, in Fig. 2 we plot the average energy for the 30 states considered against the parameter α , with $\alpha = \beta$. The values corresponding to Radau, valence and optimal coordinates are marked with circles in this graph. As is seen, optimal coordinates are located at $\alpha = \beta = -4.0^\circ$ and they are considerably superior to valence and especially to Radau coordinates. We have checked that these optimal values of the external parameters hardly change when the number of basis functions and/or the number of levels used in the optimization are increased. Also the minima for most of the individual levels considered appear at $\alpha = \beta = -4.0^\circ$, as shown in Fig. 3 where the variations in the unconverged energies with α for the $N=3$ block states are plotted.

In Table II, we include the SO_2 unconverged vibrational energies which are computed by using different coordinate systems together with the exact values, and in Fig. 4 we plot the differences between the Radau, valence, and optimal unconverged energies and the exact energies. As can be seen, Radau coordinates, with an average energy of 4132.90 cm^{-1} compared with the exact average energy of 4055.04 cm^{-1} , are the ones which gives the poorest convergence for the vibrational energies, especially in the states containing an appreciable excitation in the bend for which the differences between the unconverged and the exact energies go very

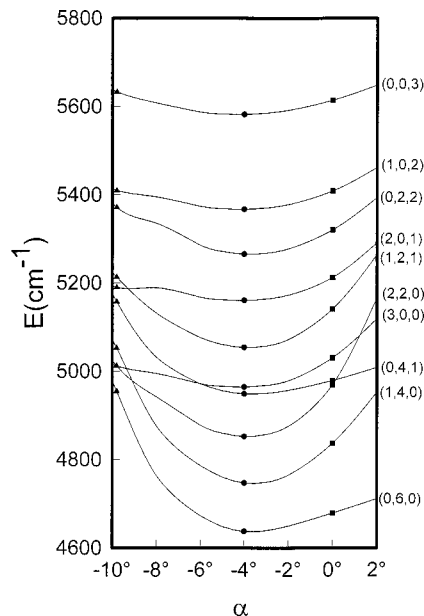


FIG. 3. The variation of the vibrational energies of SO_2 belonging to the $N=3$ block, with respect to the external parameter α , with $\alpha = \beta$. Triangles correspond to Radau coordinates, squares to valence coordinates, and circles to optimal internal coordinates.

high. Valence coordinates, with an average energy of 4083.89 cm^{-1} are better, but still a long way short of the excellent description provided by the optimal coordinates. In fact, the vibrational energies obtained using optimal coordinates with the small set of 60 anharmonic basis functions are in excellent agreement with the exact energies, as is shown by the less than 2 cm^{-1} difference between the average energy for the optimal coordinates, 4056.78 cm^{-1} , and the average value of the exact energies, 4055.04 cm^{-1} . Additional evidence of the superior quality of the optimal coordinates is given in Fig. 5, where the vibrational energies for the (0,6,0), (3,0,0), and (0,0,3) overtones of SO_2 are plotted against the variational basis set size. The convergence in energies for these three states is clearly faster for optimal internal coordinates than for Radau and valence coordinates.

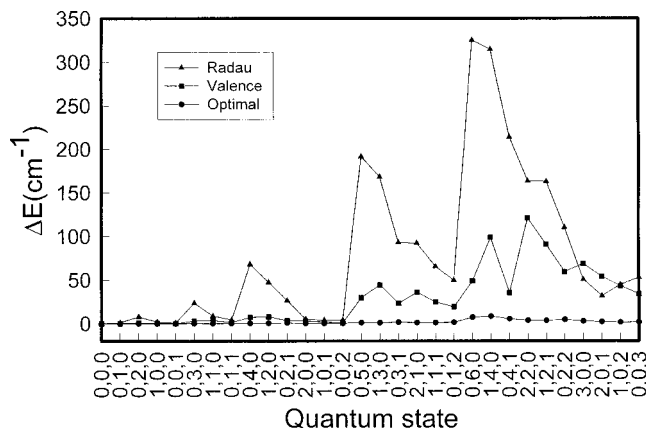
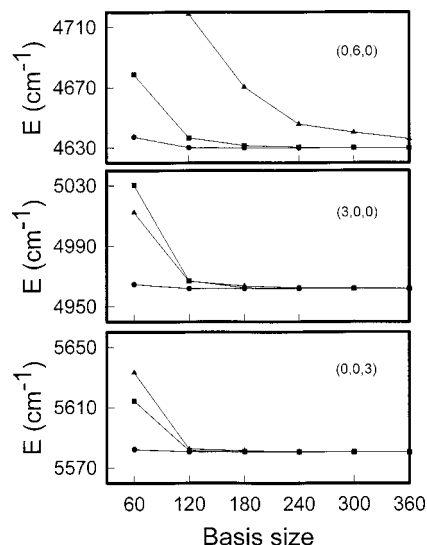
In a previous study⁵⁰ we successfully used a set of normal rotated coordinates based on the S–O₂ Jacobi arrangement to describe the vibrational motions of the SO_2 molecule. It therefore becomes interesting to compare these normal rotated Jacobi coordinates with the optimal internal coordinates derived above. In the sixth column of Table II we give the unconverged vibrational energies which are obtained for SO_2 by using the normal rotated Jacobi coordinates. The differences between the optimal and normal unconverged energies and the exact energies are also plotted in Fig. 6. The normal coordinates, with an average unconverged energy of 4076.24 cm^{-1} , are better than both Radau and valence coordinates, but as seen in Fig. 6, they are still inferior in quality to the optimal internal coordinates.

III. POTENTIAL ENERGY SURFACE

We now apply the optimal coordinates obtained for SO_2 to determine a potential energy surface for this molecule by fitting it to the experimental vibrational energies. In this re-

TABLE II. Unconverged vibrational energies (in cm^{-1}) of SO_2 for different generalized internal coordinate systems.

N^a	v_1, v_2, v_3	Radau -9.7 ^{od}	Optimal -4.0 ^o	Valence 0 ^o	Normal ^b	Exact ^c
0.0	0,0,0	1528.92	1528.80	1528.81	1528.81	1528.80
0.5	0,1,0	2048.12	2046.95	2047.04	2047.03	2046.94
1.0	0,2,0	2572.45	2564.58	2565.56	2564.81	2564.56
1.0	1,0,0	2682.29	2680.44	2681.01	2680.48	2680.43
1.0	0,0,1	2891.30	2890.45	2890.71	2891.92	2890.44
1.5	0,3,0	3105.33	3081.78	3084.64	3082.55	3081.66
1.5	1,1,0	3204.37	3195.70	3199.11	3196.67	3195.65
1.5	0,1,1	3409.06	3404.71	3406.00	3414.93	3404.65
2.0	0,4,0	3666.27	3598.63	3605.43	3607.06	3598.25
2.0	1,2,0	3757.65	3710.82	3718.30	3716.21	3710.37
2.0	0,2,1	3944.72	3919.05	3921.67	3935.03	3918.27
2.0	2,0,0	3829.86	3825.00	3827.94	3827.69	3824.78
2.0	1,0,1	4032.23	4028.59	4030.10	4036.50	4028.36
2.0	0,0,2	4245.16	4241.45	4241.83	4252.77	4241.02
2.5	0,5,0	4306.18	4115.44	4144.20	4127.83	4114.34
2.5	1,3,0	4392.94	4225.57	4268.93	4234.31	4224.60
2.5	0,3,1	4524.37	4432.88	4454.66	4473.92	4431.32
2.5	2,1,0	4429.30	4338.17	4372.89	4343.00	4337.04
2.5	1,1,1	4605.13	4540.68	4564.33	4559.85	4539.65
2.5	0,1,2	4801.02	4752.86	4770.74	4787.44	4751.33
3.0	0,6,0	4955.31	4637.40	4678.81	4661.66	4629.93
3.0	1,4,0	5053.19	4746.94	4837.18	4760.19	4738.36
3.0	0,4,1	5158.14	4949.30	4979.22	5001.14	4943.81
3.0	2,2,0	5012.45	4852.59	4969.78	4861.79	4848.82
3.0	1,2,1	5213.56	5054.02	5141.23	5084.92	5050.37
3.0	0,2,2	5371.33	5265.75	5320.43	5322.24	5261.00
3.0	3,0,0	5012.45	4964.75	5030.50	4966.67	4961.84
3.0	2,0,1	5190.49	5160.71	5212.60	5175.16	5158.69
3.0	1,0,2	5410.05	5367.10	5408.65	5394.51	5365.49
3.0	0,0,3	5633.38	5582.21	5614.49	5750.10	5580.56
$\langle E \rangle$		4132.90	4056.78	4083.89	4076.24	4055.04

^a $N = v_1 + v_3 + v_2/2$.^bCalculated using normal rotated S-O₂ Jacobi coordinates. See Ref. 50.^cResults obtained using a basis set large enough to converge all the energies included in this table.^d $\alpha = \beta$.FIG. 4. Differences between unconverged and exact vibrational energies of SO_2 for different internal coordinate systems.FIG. 5. The variation of selected vibrational energies of SO_2 with respect to the basis set size. Triangles correspond to Radau coordinates, squares to valence coordinates, and circles to optimal internal coordinates.

spect, we follow the same strategy used successfully in our previous works on N_2O ,⁴¹ CO_2 ,⁴² and OCS .⁴⁵ The potential energy surface is represented by a valence Morse-cosine potential expansion which, for the case of bent triatomic molecules such as SO_2 , takes the form

$$V(y_1, y_2, y_3) = \sum M_{ij} y_i y_j + \sum M_{ijk} y_i y_j y_k + \sum M_{ijkl} y_i y_j y_k y_l + \dots, \quad (6)$$

where

$$y_1 = 1 - e^{-a_1(R_1 - R_{1,e})}, \quad (7)$$

$$y_2 = \cos \theta - \cos \theta_e, \quad (8)$$

$$y_3 = 1 - e^{-a_3(R_2 - R_{2,e})}. \quad (9)$$

The initial values of the coefficients M are computed from a given set of force constants of the molecule by using the analytical expressions which are obtained from the re-

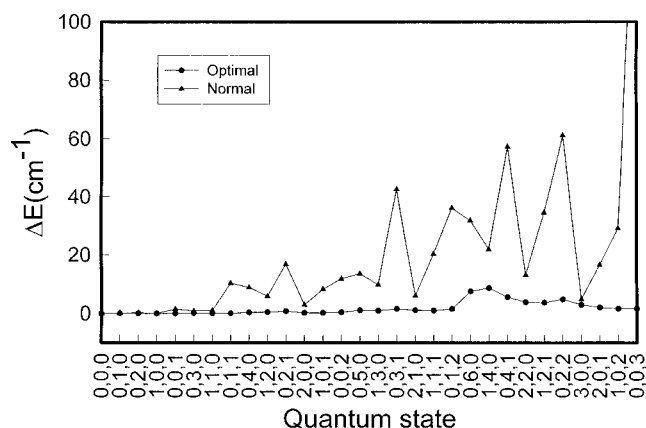
FIG. 6. Differences between unconverged and exact vibrational energies of SO_2 for normal rotated Jacobi coordinates and optimal internal coordinates.

TABLE III. Force constants (aJ/Å/radian) and equilibrium distances (Å) for the SO₂ molecule.

Parameter	Martin ^a	Fitted MC ^b
f_{rr}	10.232 92	10.293 87
$f_{rr'}$	0.003 17	-0.018 58
f_{aa}	1.655 01	1.656 68
f_{ra}	0.241 95	0.248 06
f_{rrr}	-68.935 53	-70.687 98
$f_{rrr'}$	-0.531 80	-0.751 70
f_{rra}	-0.878 70	-0.947 49
$f_{rr'a}$	-0.691 03	-0.680 10
f_{raa}	-1.841 66	-1.922 06
f_{aaa}	-2.171 55	-2.095 74
f_{rrrr}	378.788 00	396.538 85
$f_{rrrr'}$	0.761 15	2.344 94
$f_{rrr'r'}$	3.591 59	4.854 98
f_{rrra}	1.404 72	1.709 51
$f_{rrr'a}$	2.280 35	2.328 49
f_{rraa}	0.412 95	0.549 08
$f_{rr'aa}$	2.967 61	3.062 26
f_{raaa}	3.450 25	3.589 70
f_{aaaa}	4.487 18	4.217 06
R_e (Å)	1.437 16	1.4307 82
α_e (degrees)	119.25	119.3297

^aFrom Ref. 16.^bThe equilibrium geometry is taken from Ref. 29.

expansion of the Morse-cosine potential function in terms of the displacement valence coordinates. These analytical expressions up to the fourth order for bent symmetrical triatomic molecules are given in the Appendix. The Morse constants a_i are calculated by canceling out the cubic Morse coefficients, i.e., by taking $M_{iii}=0$. This condition leads to the usual expression $a_i = -f_{iii}/3f_{ii}$, where f stands for the stretching valence force constants. The Morse-cosine potential energy surface thus obtained is then used as the starting point for carrying out the adjustment of the potential to the vibrational frequencies of the molecule observed spectroscopically.

The *ab initio* quartic force field for SO₂ recently determined by Martin¹⁶ at the CCSD(T)/AVQZ+1 level is used as the starting point for carrying out the adjustment. This choice is guided by the increasing evidence that *ab initio* force fields constitute excellent options for initiating potential energy function fits.^{51–54,45} The force constants and the equilibrium geometry for the SO₂ Martin force field are given in the second column of Table III. Use of these force constants in Eqs. (A2) given in the Appendix provides us with the initial values of the M Morse-cosine expansion coefficients. We employ here the most recent experimental equilibrium geometry determined by Flaud and Lafferty²⁹ instead of the *ab initio* equilibrium geometry computed by Martin, since no rotational information is used in the adjustment. The initial values of coefficients M and the Morse constants a_i are given in the second column of Table IV.

Before going through the adjustment it is important to check how good the starting potential energy function is at describing the vibrational frequencies of the molecule. In Table V we compare the vibrational frequencies which are computed for SO₂ by using the Morse-cosine potential ex-

TABLE IV. Coefficients (in aJ) of the Morse-cosine expansions for the SO₂ molecule. The equilibrium geometry is $R_e=1.430782$ Å and $\theta_e=119.3297^\circ$.

Parameter	Martin MC potential	Fitted MC potential
$M_{11}=M_{33}$	1.014 670	0.982 329
M_{13}	0.000 628 658	-0.003 546 4
M_{22}	1.088 733	1.089 830
$M_{12}=M_{23}$	-0.123 589	-0.132 430 3
$M_{111}=M_{333}$		
$M_{113}=M_{133}$	-0.023 168 6	-0.033 111 5
$M_{112}=M_{233}$	0.038 146 1	0.041 560 4
M_{123}	0.157 191	0.148 888
$M_{122}=M_{223}$	-0.499 696	-0.512 332
M_{222}	-0.155 460	-0.175 235
$M_{1111}=M_{3333}$	0.028 829 0	0.028 829 0
$M_{1113}=M_{1333}$	-0.018 284 1	-0.018 284 1
M_{1133}	0.011 987 5	0.011 987 5
$M_{1112}=M_{2333}$	0.035 028 0	0.035 028 0
$M_{1123}=M_{1233}$	-0.036 904 0	-0.036 904 0
$M_{1122}=M_{2233}$	-0.255 116	-0.255 116
M_{1223}	0.336 501	0.336 501
$M_{1222}=M_{2223}$	-0.091 522 1	-0.091 522 1
M_{2222}	0.838 353	0.838 353
$a_1=a_3$ (Å ⁻¹)	2.245 55	2.289 00

pansion derived previously from the *ab initio* Martin force field, to the spectroscopically observed values. We also include in this table the vibrational frequencies corresponding to the full variational Kauppi and Halonen (KH-FV) potential.^{12,17} Notice that, except for the states excited in the antisymmetric stretch, there is an excellent, nearly spectroscopic, agreement between the vibrational frequencies computed using the *ab initio* Martin Morse-cosine (M-MC) potential and the observed values, which is similar to that provided by the empirical KH-FV potential. The SO₂ *ab initio* M-MC potential function therefore gives an excellent description of the vibrational motions of the molecule, according to the current standards in the electronic calculations. Consequently the main task of the fit basically consists in correcting the potential energy function deficiency associated with the antisymmetric stretching normal mode.

The adjustment is carried out by varying the coefficients M and the Morse parameters a_i until the standard deviation in the vibrational frequencies is minimized. The cubic coefficients M_{iii} are however kept to their original zero values because allowing them to vary gives rise to unphysical minima inside the repulsive potential regions. The input data used in the fit are the 18 vibrational band origins measured by Flaud *et al.*^{28–32} and Guelachvili²⁵ using high resolution Fourier transform spectroscopy. Shelton *et al.*²² and Brand *et al.*²³ have reported more experimental vibrational band origins for low-lying states of SO₂, but their uncertainties are much higher and they were not included in the fit. The standard deviation in the vibrational frequencies is minimized by using the nonlinear least squares method based on the conjugate gradient algorithm. The transition energies are computed by using a basis set of 500 product-type anharmonic functions constructed as stated in Sec. II with a maxi-

TABLE V. A comparison between calculated and observed vibrational frequencies (in cm^{-1}) for the SO_2 molecule. Results for the full variational Kauppi-Halonen (KH-FV) and the *ab initio* Martin Morse-cosine (M-MC) potential energy functions.

v_1, v_2, v_3	KH-FV		M-MC		Observed ^b	v_1, v_2, v_3	KH-FV		M-MC		Observed ^b
	Calc.	Diff. ^a	Calc.	Diff.			Calc.	Diff. ^a	Calc.	Diff.	
0,1,0	518.15	-0.28	517.80	0.07	517.87	0,3,2	4241.25	0.25	4232.15	9.35	4241.50
0,2,0	1035.76	-0.63	1034.97	0.16	1035.13	2,4,0	4342.22	0.48	4336.71	5.99	4342.70
1,0,0	1151.63	0.08	1150.58	1.13	1151.71	1,1,2	4344.09		4335.23		
0,0,1	1361.64	0.42	1357.28	4.78	1362.06	0,6,1	4438.34		4429.59		
0,3,0	1552.87	-1.13	1551.40	0.35	1551.75	3,2,0	4451.12	-4.22	4446.73	0.17	4446.9
1,1,0	1666.85	-0.52	1665.31	1.02	1666.33	1,4,1	4541.41		4533.87		
0,1,1	1875.85	-0.05	1871.12	4.68	1875.80	0,1,3	4558.21		4546.66		
0,4,0	2069.46	-2.59	2067.00	-0.13	2066.87	4,0,0	4562.84	-2.74	4559.04	1.06	4560.1
1,2,0	2181.57	-1.24	2179.42	0.91	2180.33	0,9,0	4644.93		4628.62		
2,0,0	2295.98	-0.17	2293.95	1.86	2295.81	2,2,1	4646.03		4639.20		
0,2,1	2389.47	-0.55	2384.37	4.55	2388.92	1,7,0	4747.99		4737.36		
1,0,1	2499.57	0.30	2494.59	5.28	2499.87	0,4,2	4749.71		4740.17		
0,5,0	2582.55	-0.25	2581.65	0.65	2582.30	3,0,1	4752.66	-1.43	4746.67	4.56	4751.23
1,3,0	2695.81	-2.18	2692.84	0.79	2693.63	1,2,2	4850.82	-2.68	4841.51	6.63	4848.14
0,0,2	2712.23	1.15	2704.20	9.18	2713.38	2,5,0	4852.70		4845.46		
2,1,0	2808.24	-1.05	2805.61	1.58	2807.19	0,7,1	4949.18		4938.40		
0,3,1	2902.53		2896.95			2,0,2	4953.30		4945.00		
1,1,1	3010.85	-0.53	3005.33	4.99	3010.32	3,3,0	4959.49	-1.49	4954.13	3.87	4958.0
0,6,0	3101.13		3095.26			1,5,1	5050.53		5041.82		
1,4,0	3209.56		3205.44			0,2,3	5063.96		5052.11		
0,1,2	3222.53	-0.28	3214.07	8.18	3222.25	4,1,0	5069.06	1.24	5064.57	5.73	5070.3
2,2,0	3320.04		3316.68			2,3,1	5153.31		5145.73		
0,4,1	3415.02		3408.75			0,10,0	5158.54		5136.86		
3,0,0	3433.05	-1.86	3430.10	1.09	3431.19	1,0,3	5163.02	2.62	5152.24	13.40	5165.64
1,2,1	3521.58		3515.52			0,5,2	5257.43	4.47	5247.38	14.52	5261.9
0,7,0	3616.23		3607.70			3,1,1	5257.97		5251.26		
2,0,1	3629.90	-0.14	3624.39	5.37	3629.76	1,8,0	5260.00		5245.64		
1,5,0	3722.85		3717.14			1,3,2	5356.99		5347.19		
0,2,2	3732.20	-1.30	3723.42	7.48	3730.90	2,6,0	5362.71		5353.24		
2,3,0	3831.35		3827.08			0,0,4	5380.27		5366.94		
1,0,2	3836.69	0.37	3828.48	8.58	3837.06	2,1,2	5457.74		5448.68		
0,5,1	3926.95		3919.67			0,8,1	5459.49		5445.98		
3,1,0	3942.31	-2.41	3938.70	1.20	3939.90	3,4,0	5467.46	-1.86	5460.78	4.82	5465.6
1,3,1	4031.76	-2.37	4025.07	4.32	4029.39	...					
0,0,3	4051.76	2.24	4040.74	13.26	4054.00	5,1,0	6188.48	2.22	6183.21	7.49	6190.7
0,8,0	4130.83		4118.85			...					
2,1,1	4138.23		4132.06			1,0,4	6478.54	10.66	6465.88	23.32	6489.2
1,6,0	4235.66		4227.82								

^aDiff.=Obs.-Calc.^bThe observed values are taken from Refs. 22–25, 28–32.

num of 12 one-dimensional anharmonic wavefunctions for the stretches and 24 for the bend. These variational specifications guarantee a convergence to within 0.001 cm^{-1} in all vibrational frequencies included in the adjustment.

The parameters of the Morse-cosine potential function fitted for SO_2 are given in the third column of Table IV. In Table VI we compare the vibrational frequencies calculated using this potential with the spectroscopically observed values. As observed, the potential energy function determined practically reproduces, up to the second decimal place, the observed vibrational frequencies for all the vibrational states included in the fit. This accuracy is assessed by the standard deviation obtained in the frequencies for these states, which goes from the initial value of 4.92 cm^{-1} for the Martin MC potential to the final value of just 0.02 cm^{-1} for the fitted MC potential. For the states not included in the fit, there is also a reasonably good agreement between the computed and the observed frequencies if we bear in mind the lower reso-

lution of the band origins for these states. In Table VII we give the harmonic normal frequencies corresponding to the fitted MC potential together with the *ab initio* values computed by Martin¹⁶ and the empirical values obtained by Yamanouchi *et al.*²⁷ and by Lafferty *et al.*²⁸ from their normal mode analyses of the observed energies. The *ab initio* harmonic frequency for the antisymmetrical normal stretch deviates the most from the empirical values. This is in accordance with the poor description provided by the Martin MC potential of the antisymmetric stretching normal mode, as previously noticed from the results of Table V. The fit then properly corrects the three harmonic normal frequencies giving values for them which are in excellent agreement with those determined empirically. In the last column of Table III we also list the force constants for the fitted MC potential, which are directly calculated from the Morse-cosine expansion coefficients by using the analytical expressions (A3) given in the Appendix. These empirical force constants are

TABLE VI. A comparison between calculated (using the fitted Morse-cosine potential energy function) and observed vibrational frequencies (in cm^{-1}) for the SO_2 molecule.

v_1, v_2, v_3	Calculated	Observed ^a	Obs.–Calc.	Dunham ^b	Dun.–Calc.	v_1, v_2, v_3	Calculated	Observed ^a	Obs.–Calc.	Dunham ^b	Dun.–Calc.
0,1,0	517.91	517.87*	−0.04	517.83	−0.08	0,3,2	4240.37	4241.50	1.13	4240.70	0.33
0,2,0	1035.17	1035.13*	−0.04	1034.92	−0.25	2,4,0	4337.32	4342.70	5.38	4337.20	−0.12
1,0,0	1151.69	1151.71*	0.02	1151.70	0.01	1,1,2	4343.80			4344.26	0.46
0,0,1	1362.07	1362.06*	−0.01	1362.36	0.29	0,6,1	4433.62			4433.92	0.30
0,3,0	1551.68	1551.75*	0.07	1551.25	−0.43	3,2,0	4448.02	4446.9	1.88	4448.37	0.35
1,1,0	1666.34	1666.33*	−0.01	1666.36	0.02	1,4,1	4537.85			4537.60	−0.25
0,1,1	1875.80	1875.80*	0.00	1876.07	0.27	0,1,3	4559.39			4560.06	0.67
0,4,0	2067.35	2066.87	−0.48	2066.82	−0.53	4,0,0	4561.31	4560.1	−1.21	4561.52	0.21
1,2,0	2180.35	2180.33*	−0.02	2180.27	−0.08	0,9,0	4629.43			4632.94	3.51
2,0,0	2295.81	2295.81*	0.00	2295.88	0.07	2,2,1	4643.58			4643.52	−0.06
0,2,1	2388.93	2388.92*	−0.01	2389.08	0.15	1,7,0	4737.63			4738.13	0.50
1,0,1	2499.85	2499.87*	0.02	2499.95	0.10	0,4,2	4748.03			4748.27	0.24
0,5,0	2582.07	2582.30	0.23	2581.62	−0.45	3,0,1	4751.80	4751.23	−0.57	4751.59	−0.21
1,3,0	2693.64	2693.63*	−0.01	2693.41	−0.23	2,5,0	4845.72			4845.56	−0.16
0,0,2	2713.40	2713.38*	−0.02	2713.97	0.57	1,2,2	4849.54	4848.14	−1.40	4849.90	0.36
2,1,0	2807.20	2807.19*	−0.01	2807.37	0.17	0,7,1	4942.32			4943.29	0.97
0,3,1	2901.38			2901.38	0.00	2,0,2	4953.55			4953.80	0.25
1,1,1	3010.30	3010.32*	0.02	3010.45	0.15	3,3,0	4954.89	4958.0	3.11	4955.13	0.24
0,6,0	3095.75			3095.64	−0.11	1,5,1	5045.45			5045.18	−0.27
1,4,0	3206.11			3205.76	−0.35	0,2,3	5064.30			5064.86	0.56
0,1,2	3222.95	3222.25	−0.70	3223.54	0.59	4,1,0	5066.19	5070.3	4.11	5066.68	0.49
2,2,0	3317.97			3318.10	0.13	0,10,0	5137.82			5143.76	5.94
0,4,1	3413.04			3412.96	−0.08	2,3,1	5149.57			5149.33	−0.24
3,0,0	3432.36	3431.19	−1.17	3432.49	0.13	1,0,3	5164.75	5165.64	0.89	5165.55	0.80
1,2,1	3520.18			3520.22	0.04	1,8,0	5245.82			5247.31	1.49
0,7,0	3608.27			3608.87	0.60	0,5,2	5254.87	5261.9	7.03	5255.16	0.29
2,0,1	3629.77	3629.76*	−0.01	3629.71	−0.06	3,1,1	5255.72			5255.65	−0.07
1,5,0	3717.67			3717.36	−0.31	2,6,0	5353.11			5353.13	0.02
0,2,2	3731.97	3730.90	−1.07	3732.46	0.49	1,3,2	5354.71			5354.85	0.14
2,3,0	3828.04			3828.05	0.01	0,0,4	5383.88			5384.18	0.30
1,0,2	3837.54	3837.06	−0.48	3837.96	0.42	0,8,1	5449.81			5451.90	2.09
0,5,1	3923.82			3923.81	−0.01	2,1,2	5456.53			5456.84	0.31
3,1,0	3940.49	3939.90	−0.59	3940.82	0.33	3,4,0	5460.99	5465.6	4.61	5461.08	0.09
1,3,1	4029.39	4029.39*	0.00	4029.28	−0.11	...					
0,0,3	4054.00	4054.00*	0.00	4054.64	0.64	5,1,0	6184.31	6190.7	6.39	6184.90	0.59
0,8,0	4119.54			4121.31	1.77	...					
2,1,1	4136.95			4136.98	0.03	1,0,4	6481.46	6489.2	7.74	6482.51	1.05
1,6,0	4228.21			4228.15	−0.06						

^aThe frequencies marked with an asterisk are those used in the fit.^bResults obtained using the Dunham-type expansion derived by Yamanouchi *et al.* (Ref. 27) from observed vibrational frequencies.

expected to be more reliable than the previous ones^{1,5} considering the high accuracy of the MC potential energy surface obtained and the closeness of it to the *ab initio* force field from which it was derived.

As an additional check of the quality of the Morse-cosine potential energy function determined for SO_2 , we compare the vibrational frequencies calculated by using this potential with those obtained from the Dunham-type expansion derived by Yamanouchi *et al.*²⁷ by fitting a very large

number of observed vibrational levels, most of them extracted from the dispersed fluorescence spectra of the \tilde{C}^1B_2 electronic state of the molecule. The Dunham vibrational frequencies and the differences between them and the calculated frequencies are given in the two last columns of Table VI. As observed, the differences stay below 1 cm^{-1} in absolute values for nearly all states, with the noticeable exception of those which are very excited in the bending normal mode. These discrepancies in the excited bending states are also present, to a larger extent, in the vibrational frequencies calculated from the Kauppi and Halonen potential, as can be seen by comparing the results in the first column of Table V with the Dunham frequencies given in Table VI. From this it is clear that the availability of accurate experimental information on the bending overtones of SO_2 would be of great help in achieving further improvements in the potential energy function of the molecule.

In Fig. 7 we finally show the contour plots of the adjusted SO_2 Morse-cosine potential function in valence coor-

TABLE VII. Harmonic normal frequencies (cm^{-1}) for the SO_2 molecule.

	ω_1	ω_2	ω_3
Martin ^a	1166.056	519.503	1376.171
Yamanouchi <i>et al.</i> ^b	1167.84	522.21	1382.18
Lafferty <i>et al.</i> ^c	1167.904	522.213	1381.816
Fitted Morse-cosine potential	1167.710	522.270	1382.000

^aFrom Ref. 16.^bFrom Ref. 27.^cFrom Ref. 28.

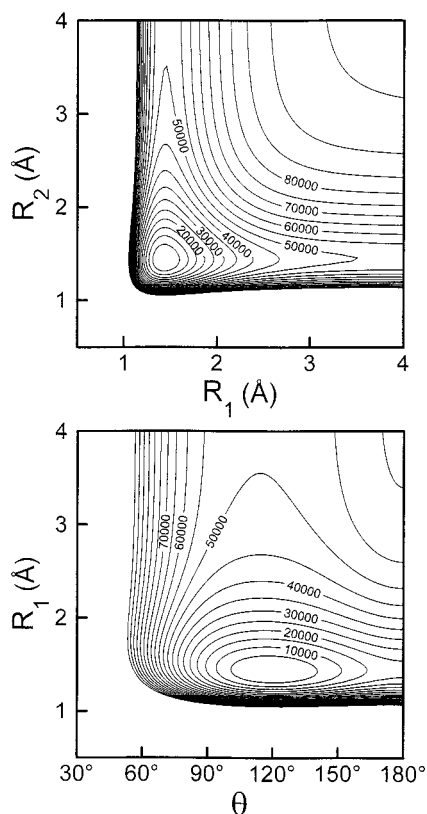


FIG. 7. Contour plots for the fitted Morse-cosine potential energy function of SO_2 in valence coordinates, with θ and R_1 fixed at their equilibrium values.

ordinates, with the angular and radial coordinates fixed at their equilibrium values. The dissociation energy D_e for this potential is found to be $50\,863.29\text{ cm}^{-1}$ and, by subtracting from it the zero-point energy, 1529.32 cm^{-1} , a value for D_0 of $49\,333.97\text{ cm}^{-1}$ is obtained, which is not much higher than the recently measured experimental value of $45\,725.3\text{ cm}^{-1}$.⁵⁵ Furthermore, the use of the cosine variable to represent the bending motion in the potential energy expansion allows us to describe properly the barrier to linearity ($\theta = 180^\circ$) for SO_2 , which is found to be located at the radial distances $R_1 = R_2 = 1.4451\text{ Å}$ with a height of $18\,215.80\text{ cm}^{-1}$ above the minimum of the potential.

IV. CONCLUSIONS

In this paper we carry out a variational optimization of the generalized internal vibrational coordinates for the electronic ground state of the SO_2 molecule. The optimal coordinates obtained are found to be clearly superior to valence and Radau coordinates, and also to a set of curvilinear normal Jacobi coordinates previously derived. These optimal coordinates are then used to determine a new potential energy function for SO_2 by fitting it to the experimental vibrational frequencies of the molecule and by computing variationally the corresponding transition energies. The potential energy function is represented by a fourth-order Morse-cosine expansion in valence coordinates and the initial values of the expansion coefficients are calculated directly from

the force constants of an *ab initio* potential surface computed by Martin at the CCSD(T) level. The potential energy function determined reproduces accurately the observed vibrational frequencies of the SO_2 electronic ground state and behaves well for large values of the vibrational coordinates.

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APPENDIX: ANALYTICAL EXPRESSIONS RELATING MORSE-COSINE COEFFICIENTS TO VALENCE FORCE CONSTANTS

The usual fourth-order polynomial expansion of the potential energy function is

$$V(r_1, r_2, r_3) = \frac{1}{2} \sum f_{ij} r_i r_j + \frac{1}{6} \sum f_{ijk} r_i r_j r_k + \frac{1}{24} \sum f_{ijkl} r_i r_j r_k r_l, \quad (\text{A1})$$

where $r_1 = R_1 - R_{1,e}$, $r_2 = \theta - \theta_e$ and $r_3 = R_2 - R_{2,e}$, and f are the valence force constants. Then, by re-expanding the Morse-cosine potential energy function (6) in terms of the displacement variables r_i ($i = 1-3$), we find the following analytical expressions relating the Morse-cosine expansion coefficients M to the valence force constants f :

$$\begin{aligned} M_{ii} &= \frac{f_{ii}}{2a_i^2}, \\ M_{ij} &= \frac{f_{ij}}{a_i a_j}, \\ M_{22} &= \frac{f_{22}}{2 \sin^2 \theta_e}, \\ M_{i2} &= -\frac{f_{i2}}{a_i \sin \theta_e}, \\ M_{iii} &= \frac{f_{iii} + 3a_i f_{ii}}{6a_i^3}, \\ M_{iij} &= \frac{f_{iij} + a_i f_{ij}}{2a_i^2 a_j}, \\ M_{ii2} &= -\frac{f_{ii2} + a_i f_{i2}}{2a_i^2 \sin \theta_e}, \\ M_{i2j} &= -\frac{f_{i2j}}{a_i a_j \sin \theta_e}, \end{aligned} \quad (\text{A2})$$

$$\begin{aligned}
M_{i22} &= \frac{f_{i22} - f_{i2} \cot \theta_e}{2a_i \sin^2 \theta_e}, \\
M_{222} &= -\frac{f_{222} - 3f_{22} \cot \theta_e}{6 \sin^3 \theta_e}, \\
M_{iii} &= \frac{f_{iii} + 6a_i f_{iii} + 11a_i^2 f_{ii}}{24a_i^4}, \\
M_{iiij} &= \frac{f_{iiij} + 3a_i f_{iiij} + 2a_i^2 f_{ij}}{6a_i^3 a_j}, \\
M_{iijj} &= \frac{f_{iijj} + a_i f_{ijj} + a_j f_{iij} + a_i a_j f_{ij}}{4a_i^2 a_j^2}, \\
M_{iii2} &= -\frac{f_{iii2} + 3a_i f_{ii2} + 2a_i^2 f_{i2}}{6a_i^3 \sin \theta_e}, \\
M_{ii2j} &= -\frac{f_{ii2j} + a_i f_{i2j}}{2a_i^2 a_j \sin \theta_e}, \\
M_{ii22} &= \frac{f_{ii22} + a_i f_{i22} - (f_{ii2} + a_i f_{i2}) \cot \theta_e}{4a_i^2 \sin^2 \theta_e}, \\
M_{i22j} &= \frac{f_{i22j} - f_{i23} \cot \theta_e}{2a_i a_j \sin^2 \theta_e}, \\
M_{i222} &= -\frac{f_{i222} - 3f_{i22} \cot \theta_e + 3f_{i2} \cot^2 \theta_e + f_{i2}}{6a_i \sin^3 \theta_e}, \\
M_{2222} &= \frac{f_{2222} - 6f_{222} \cot \theta_e + 15f_{22} \cot^2 \theta_e + 4f_{22}}{24 \sin^4 \theta_e},
\end{aligned}$$

where $i, j = 1, 3$ and $i \neq j$. By now inverting the above relations we obtain

$$\begin{aligned}
f_{ii} &= 2a_i^2 M_{ii}, \\
f_{22} &= 2M_{22} \sin^2 \theta_e, \\
f_{ij} &= a_i a_j M_{ij}, \\
f_{i2} &= -a_i M_{i2} \sin \theta_e, \\
f_{iii} &= 6a_i^3 (M_{iii} - M_{ii}), \\
f_{iiij} &= a_i^2 a_j (2M_{iiij} - M_{ij}), \\
f_{ii2} &= a_i^2 (-2M_{ii2} + M_{i2}) \sin \theta_e, \\
f_{i2j} &= -a_i a_j M_{i2j} \sin \theta_e, \\
f_{i22} &= a_i (2M_{i22} \sin^2 \theta_e - M_{i2} \cos \theta_e), \\
f_{222} &= -6(M_{222} \sin^2 \theta_e - M_{22} \cos \theta_e) \sin \theta_e, \\
f_{iiii} &= 2a_i^4 (12M_{iiii} - 18M_{iii} + 7M_{ii}), \\
f_{iiij} &= a_i^3 a_j (6M_{iiij} - 6M_{iij} + M_{ij}), \\
f_{iijj} &= a_i^2 a_j^2 (4M_{iijj} - 2M_{iij} - 2M_{ijj} + M_{ij}),
\end{aligned} \tag{A3}$$

$$\begin{aligned}
f_{iii2} &= -a_i^3 (6M_{iii2} - 6M_{ii2} + M_{i2}) \sin \theta_e, \\
f_{ii2j} &= a_i^2 a_j (-2M_{ii2j} + M_{i2j}) \sin \theta_e, \\
f_{ii22} &= a_i^2 [(-2M_{ii2} + M_{i2}) \cos \theta_e \\
&\quad + 2(2M_{ii22} - M_{i22}) \sin^2 \theta_e], \\
f_{i22j} &= a_i a_j (2M_{i22j} \sin^2 \theta_e - M_{i2j} \cos \theta_e), \\
f_{i222} &= a_i (-6M_{i222} \sin^2 \theta_e + 6M_{i22} \cos \theta_e + M_{i2}) \sin \theta_e, \\
f_{2222} &= 24M_{2222} \sin^4 \theta_e - 36M_{222} \cos \theta_e \sin^2 \theta_e \\
&\quad - 8M_{22} \sin^2 \theta_e + 6M_{22} \cos^2 \theta_e.
\end{aligned}$$

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