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Rotational spectrum of SO$_3$ and theoretical evidence for the formation of sixfold rotational energy-level clusters in its vibrational ground state

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The structure of the purely rotational spectrum of sulphur trioxide $^{32}$S$^{16}$O$_3$ is investigated using a new synthetic line list. The list combines line positions from an empirical model with line intensities determined, in the form of Einstein coefficients, from variationally computed ro-vibrational wavefunctions in conjunction with an \textit{ab initio} dipole moment surface. The empirical model providing the line positions involves an effective, Watsonian-type rotational Hamiltonian with literature parameter values resulting from least-squares fittings to observed transition frequencies. The formation of so-called 6-fold rotational energy clusters at high rotational excitation are investigated. The SO$_3$ molecule is planar at equilibrium and exhibits a unique type of rotational-energy clustering associated with unusual stabilization axes perpendicular to the S–O bonds. This behaviour is characterized theoretically in the $J$ range from 100–250. The wavefunctions for these cluster states are analysed, and the results are compared to those of a classical analysis in terms of the rotational-energy-surface formalism. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4882865]

I. INTRODUCTION

We have previously reported a room-temperature \textit{ab initio} line list for $^{32}$S$^{16}$O$_3$, obtained by computing wavenumbers and intensities for rovibrational transitions in the electronic ground state involving rovibrational states with $J \leq 85$ together with the term values of these states. For these calculations, we used the variational quantum-mechanical method outlined in Sec. II. The calculations were based on a potential energy surface (PES) computed entirely by \textit{ab initio} methods.

We made comparisons with the results of extensive experimental studies of this molecule, in which several line positions and relative intensities for a number of bands were recorded at room temperature. The computed spectrum generally represented the observations fairly well, albeit with minor discrepancies in the line positions, reflecting small inaccuracies in the purely \textit{ab initio} PES whose parameter values were not refined in least-squares fittings to experimental wavenumber data. As part of this previous work, we scaled a number of reliable experimental relative intensities to our absolute scale, and included these transitions in the HITRAN 2012 database.

Amongst the calculated transitions the “forbidden” rotational spectrum for this trigonal planar molecule was computed. Induced by centrifugal distortions of bond lengths and angles, these transition lines exhibit an interesting structure. Experimentally, only a handful of microwave lines have been measured. As well as these lines being few in number, no intensity values are available for them. In this paper we aim at investigating the behaviour of the rotating SO$_3$ molecule from a theoretical perspective.

As well as interpreting the rotational spectrum, we also investigate the phenomenon of near-degenerate energy cluster formation in the highly excited rotational states of SO$_3$. The analysis of the rotational motion of SO$_3$ gives us an opportunity to characterize, for the first time, such energy cluster formation for a planar tetratomic molecule containing no hydrogen.

Dorney and Watson\textsuperscript{11} were the first to explain the formation of quasi-degenerate energy levels for spherical top molecules using classical arguments followed by a series of works based on the classical description of the clustering phenomena.\textsuperscript{12–27} Most of these descriptions involve the motion of the molecule about a “localization” axis at high rotational excitation,\textsuperscript{11,15,19,22} The clustering phenomenon was further explored in great detail using a formalism based on the rotational energy surface (RES).\textsuperscript{28} In this approach, a RES is introduced to describe the classical rotational energy of the molecule as a function of the classical angular momentum vector, and equivalent, stationary points on this surface, so-called relative equilibria, in particular equivalent maxima directly associated with the patterns of rotational energy clusters. For a molecule with structural symmetry (resulting from identical nuclei arranged symmetrically at equilibrium), the rotational energy clusters are associated with the emergence of symmetrically equivalent localization axes recognizable on the RES. This behaviour provides an example of a quantum system approaching a classical limit with increasing energy. The bifurcation of stationary points is important for formation of rotational energy clusters of some types of molecules.\textsuperscript{26,29} Zhilinski\textsuperscript{25} also studied the role of symmetry in the cluster formation process in great detail. Usually a RES is obtained from an effective rotational Hamiltonian,\textsuperscript{28} which is effectively a perturbation theory expansion. Here we follow a
physically more sound approach where the classical limit is applied to the actual ro-vibrational Hamiltonian (see, for example, Refs. 26, 30, and 31) with the vibrational coordinates optimized by minimizing the classical energy at each orientation of the rotation of the molecule in question.

Typical molecules exhibiting rotational energy clusters are of the type XY\n with a heavy central atom X, Y being H or D, and the X-Y bonds being nearly orthogonal, which are often referred to as local mode molecules. The formation of rotational or ro-vibrational energy-level clusters of this type of molecules was studied for triatomic HX\n molecules (see, for example, Refs. 22 and 32–35), pyramidal \n H\n molecules, including PH\n, BiH\n, SbH\n, and their deuterated isotopologues. Molecules with heavier \\n atoms can also form rotational energy clusters. The existence of the clustering was predicted for the molecules CF\n, \n SF\n, \n P\n, and experimentally confirmed for SF\n.

For PH\n, BiH\n, and SbH\n, the energy cluster formation was (theoretically) investigated for J ≤ 70. SO\n is not a local mode molecule, but, as we will show, for SO\n a pattern of energy clusters is predicted in the present work. However, the clustering behaviour does not manifest itself until the rotational excitation reaches the J range between 100 and 250. SO\n is also much heavier than the HX\n molecules, it has much smaller rotational energy spacings and, in consequence, states with much higher J values will be populated at a given temperature. This makes the clustering states of SO\n potentially accessible experimentally at temperatures of a few hundred °C. Another potential opportunity to reach the required rotational excitations is the rotational centrifuge technique, which allows one to climb the rotational ladder up to the dissociation limit.

The present work deals with two aspects of the SO\n rotational motion. First, we compute rovibrational energies and wavefunctions using a basis set of high quality in order to simulate accurately the room-temperature microwave (rotational) spectrum and analyse its structure. In this manner, we have calculated rovibrational wavefunctions for J ≤ 85; this is shown to be adequate for simulating the spectrum at T = 298.15 K. The computed wavefunctions are used in conjunction with an ab initio dipole moment surface to obtain the room-temperature absorption intensities. These intensities were then combined with line positions obtained from an effective, Watsonian-type rotational Hamiltonian, whose parameter values have been determined in least-squares fittings to experimentally observed transition frequencies. This is expected to produce an accurate rotational line list for SO\n, which we recommend for inclusion in the HITRAN and other spectroscopic databases. Second, we describe for the first time, both classically and quantum-mechanically, the formation of rotational energy level clusters for a planar \n D\n(M)-type molecule SO\n.

II. COMPUTATIONAL DETAILS

In computing rovibrational energy levels for SO\n the TROVE procedure is used, for which the computational details are described extensively elsewhere. This procedure was also used to compute our previously published ab initio SO\n line list. Here we reiterate only a few essential details.

The rovibrational Schrödinger equation is solved variationally by diagonalizing a matrix representation of the appropriate Hamiltonian. The Hamiltonian is initially constructed as an expansion of kinetic energy and potential energy operators in terms of suitable linearized coordinates \n (i = 1, …, 5); the expansion is made around a non-rigid reference configuration as defined by the sixth coordinate \n. Thus three stretching coordinates, two symmetric bending coordinates and one out-of-plane-bending coordinate (where the motion described by this latter coordinate is the SO\n counterpart of the “umbrella-flipping” inversion motion in pyramidal molecules such as NH\n) are used to describe the internal motion of SO\n:

\[
\xi_k^i = 1 - \exp \left( -a \left( r_k^i - r_e \right) \right), \quad k = 1, 2, 3, \quad (1)
\]

\[
\xi_{4a}^i = \frac{1}{\sqrt{6}} \left( 2\alpha_1^i - \alpha_2^i - \alpha_3^i \right), \quad (2)
\]

\[
\xi_{4b}^i = \frac{1}{\sqrt{2}} \left( \alpha_2^i - \alpha_3^i \right), \quad (3)
\]

\[
\sin \tilde{\rho} = \frac{2}{\sqrt{3}} \sin \left( (\alpha_1 + \alpha_2 + \alpha_3)/6 \right), \quad (4)
\]

where \n (i = 1, 2, 3) and \n (k = 1, 2, 3) are linearized versions of the geometrically defined coordinates \n and \n with \n as the bond lengths and \n as the inter-bond angles. The kinetic energy operator is expanded numerically around the non-rigid reference configuration; for SO\n this configuration follows the out-of-plane bending motion. When the molecular geometry has \n symmetry, geometrical symmetry, \n ρ is the angle between the \n axis and any one of the S–O bonds.

The potential energy expansion used in the TROVE calculation results from transforming a pre-calculated, analytical PES, normally expressed in terms of geometrically defined coordinates such as bond lengths and inter-bond angles, to an expansion in the linearized coordinates \n (i = 1, 2, 3) and \n with \n Å. For SO\n, the “original” PES was calculated ab initio at the CCSD(T)-F12b level of theory. Once expanded, the Hamiltonian takes the following general form:

\[
H = \frac{1}{2} \sum_{a \beta} J_a G_{a \beta} J_\beta + \frac{1}{2} \sum_{a \lambda} (p_x G_{x a} + G_{x a} p_x) J_a + \frac{1}{2} \sum_{\lambda \nu} p_x G_{\lambda \nu} p_\nu + V + U. \quad (5)
\]

Here, \n (a = x, y, z) are rotational momentum operators and \n are vibrational momenta conjugate to the coordinates previously defined. The \n-values are kinetic energy factors computed numerically as part of the TROVE kinetic energy expansion. \n and \n are the molecular potential energy function and the pseudopotential resulting from the conversion of the expression for the classical energy to operator form, respectively.

The expansions of the kinetic energy operator and potential energy functions are truncated after the 6th and 8th
order terms, respectively. In order to construct a matrix representation of the Hamiltonian, matrix elements must be computed in terms of a suitable set of basis functions. We define "primitive" sets of 1D basis functions, $\phi_{n_1}$, where each set is associated with one of the vibrational coordinates $\xi_i$ or $\rho$; these functions are numerical solutions of 1D Schrödinger equations.\textsuperscript{47} The stretching and out-of-plane-bending basis functions are obtained in the Numerov-Cooley approach,\textsuperscript{52,53} while harmonic-oscillator eigenfunctions are used as in-plane bending basis functions $\phi_{n_2}$ and $\phi_{n_3}$. These primitive vibrational basis functions are then improved in a two-step contraction scheme,\textsuperscript{48} including a solution of the $J = 0$ problem. Subsequently, the eigenfunctions of the $J = 0$ Hamiltonian are used to construct the rovibrational basis functions for $J > 0$; the $J = 0$ basis functions are combined with rigid rotor functions $|J, K, \tau_{rot}\rangle$, where $K = 0, \ldots, J$ and $\tau_{rot}$ determines the rotational parity (see Ref. 54) within the so-called $J = 0$ contraction scheme:\textsuperscript{48}

$$\Phi^{(J)}_{\lambda, K, \tau_{rot}} = |J, K, \tau_{rot}\rangle \phi^{(J=0)}_{\lambda},$$

where $\phi^{(J=0)}_{\lambda}$ is a (vibrational) eigenfunction of the $J = 0$ Hamiltonian and $\lambda$ is a running number identifying the function. The functions $\Phi^{(J)}_{\lambda, K, \tau_{rot}}$ are then symmetrized; each of them generates an irreducible representation of the $D_{3h}(M)$ molecular symmetry group and the function is labelled by this irreducible representation. The symmetrization facilitates the calculation since it factorizes the Hamiltonian matrix into independent symmetry blocks, and this leads to significant savings of computer resources in the diagonalization step. It is important to note that due to the nuclear spin statistics of $^{32}\mathrm{S}^{16}\mathrm{O}_3$, which is made up entirely of zero-spin bosons, only states of $A_1'$ or $A''_v$ rovibrational symmetry in $D_{3h}(M)$ exist in nature. Thus, in order to simulate spectra of $^{32}\mathrm{S}^{16}\mathrm{O}_3$ we need only to compute the rovibrational eigenfunctions that transform accordingly. However, since the rovibrational Hamiltonian for any $J \geq 0$ employs the vibrational ($J = 0$) eigenfunctions, it is advantageous to pre-calculate the $J = 0$ matrix elements for all purely vibrational terms in Eq. (5).

Even though we can discard rovibrational states of $D_{3h}(M)$ symmetries $A_2'$, $A''_v$, $E'$, and $E''_v$, the calculation of the cluster-state wavefunctions and energies for $\mathrm{SO}_3$ is a formidable numerical problem owing to the high $J$-values, and the associated large ranges of $K$-values, that we must necessarily consider. This makes severe demands on the computational resources necessary for theoretically computing the associated rovibrational energies, and therefore reduce the accuracy of the energy calculations in a trade-off between numerical accuracy and computational expense. Our aim is to describe this cluster phenomenon qualitatively and the lack of extreme accuracy is no real problem. To this end we truncate the original basis set using the polyad number

$$P = 2(n_1 + n_2 + n_3) + n_4 + n_5 + \frac{n_6}{2},$$

which limits the size of the $J = 0$ matrix, and therefore matrices for $J > 0$. The $n_i$ are the principal quantum numbers associated with the 1D basis functions, $\phi_{n_i}$, and so they define the number of excited quanta for each vibrational mode considered and can be directly mapped onto the normal-mode quantum numbers traditionally used for labelling vibrational states.\textsuperscript{48} In setting up the matrix representations of the rovibrational Hamiltonian in the final step of the calculation, we use only basis functions for which $P \leq P_{\text{max}}$. For the current work we use polyad numbers $P_{\text{max}}$ of 12 for intensity calculations and $P_{\text{max}} = 8$ to investigate the rotational clustering effect. The latter, relatively low $P_{\text{max}}$-value is adequate for obtaining a satisfactory description of the energy-cluster formation. A similar approach was taken for the studies of $\mathrm{PH}_3$, $\mathrm{BiH}_3$, and $\mathrm{SbH}_3$.\textsuperscript{26,31,36}

### III. THE THEORETICAL MICROWAVE SPECTRUM

Figure 1 shows the simulated microwave spectrum for $^{32}\mathrm{S}^{16}\mathrm{O}_3$, computed with TROVE at $T = 298.15$ K. The spectrum consists of 3 439 transitions between all rotational states with $J \leq 85$. The transitions are subject to the selection rules $\Delta J = J' - J'' = 0$, $\pm 1 (J' + J'' \geq 1)$, and symmetry selection rules $A_1' \leftrightarrow A''_v$. The intensity of a transition between two states is given by

$$I(f \leftrightarrow i) = \frac{8\pi^3 N_A \nu_{if}}{(4\pi\epsilon_0)^2 \hbar c} \exp \left(\frac{-E_{i/kT}}{T}\right) \cdot S(f \leftrightarrow i),$$

where $I(f \leftrightarrow i)$ is the transition intensity for a transition from state $i$ with energy $E_i$ to state $f$ with energy $E_f$, with $\hbar \nu_{if} = E_f - E_i$, $Q$ is the partition function, $S(f \leftrightarrow i)$ is the line strength, which is defined by the following expression (see also Ref. 46):

$$S(f \leftrightarrow i) = g_{ns} \sum_{m_j,m_i} \sum_{A=X,Y,Z} |\langle \Psi_i^{(f)} | \mu_A | \Psi_i^{(i)} \rangle|^2,$$

with $\Psi_i^{(f)}$ and $\Psi_i^{(i)}$, respectively, as the wavefunctions of the initial and final states $i$ and $f$, $g_{ns}$ as the nuclear spin statistical weight factor, and $\mu_A$ as the electronically averaged component of the molecular dipole moment along the space-fixed axis $A = X, Y, Z$. The sum also runs over the quantum numbers $m_i$ and $m_f$ which are projections (in units of $\hbar$) of the total angular momentum vector $J$ onto the laboratory-fixed $Z$ axis for the initial and final states, respectively.

![FIG. 1. The microwave spectrum of $^{32}\mathrm{S}^{16}\mathrm{O}_3$, simulated theoretically at $T = 298.15$ K. Transitions between states with $J \leq 85$ are included; they are color-coded in the diagram to indicate the various transition types.](image-url)
The color coding in Fig. 1 distinguishes the $P_\nu$, $Q_\nu$, and $R$-branches in the spectrum. We see that in each branch, the intensities depend on $J$ in a characteristic manner. Figure 2 expands the wavenumber scale for the $R$-branch and the structures of the individual $K$ sub-bands are indicated. The intensities of the $K$ sub-bands decrease gradually as the $K$-values involved increase. SO$_3$ has $D_{3h}$ symmetry at equilibrium and, in consequence, no “permanent” dipole moment. Therefore, the transitions in Figure 1 are “forbidden,” that is, they are induced by the rotation-vibration interaction as explained, for example, in Sec. 14.1.14 of Ref. 50. The transitions satisfy the selection rules $A_\nu \leftarrow A_\nu'$ mentioned above and states of rovibrational symmetry $A_\nu$ or $A_\nu'$ occur when the value of the quantum number $K$ (which is not a “good,” rigorously defined quantum number, but which can nevertheless be conveniently used for labelling the SO$_3$ rotational energies) is a multiple of 3: $K = 0, 3, 6, \ldots$. Figure 2 shows that the strongest sub-bands have $K = 0 \leftarrow 3$ and $K = 3 \leftarrow 0$. In general, strong sub-bands satisfy $\Delta K = \pm 3$ and the band intensity decreases as $K \rightarrow J$.

Analyzing the wavefunctions we find that each wavefunction $\Psi_{J, K}^{(\nu_2, \nu_4)}$ has dominant contributions from the $\Phi_{J, K}^{(0, A_\nu)}$ basis functions with $\lambda = 1$ and thus associated with the vibrational ground state. However, there are other significant contributions associated with the $\nu_2$ and $\nu_4$ bending vibrational modes, respectively. Thus, even in the vibrational state conventionally labelled as the ground state, there is a non-negligible probability of finding the molecule with the $\nu_2$ or $\nu_4$ vibrational mode excited by one quantum.

The contributions to the eigenfunctions from the $\nu_2$ and $\nu_4$ basis states are highest at $K = 0$ and drop as $K \rightarrow J$. We can straightforwardly explain this classically. For a given $J$-value, the rotational eigenstates of SO$_3$ that we conventionally label by $K = J$ and $K = 0$ correspond to the two limiting cases of the molecule rotating about the $z$-axis (which, in configurations of $C_3v$ geometrical symmetry, coincides with the $C_3$ symmetry axis) and about axes perpendicular to the $z$ axis, respectively. A rotation about the $z$ axis preserves the high $D_{3h}(M)$ geometrical symmetry that the molecule has at equilibrium and the dipole moment vanishes at $D_{3h}(M)$-symmetry configurations, also for $K \rightarrow J$. For $K = 0$, the situation is quite different. The angular momentum vector of length $\sqrt{J(J + 1)}\hbar$ now results from rotation about axes perpendicular to the $z$ axis and this, in turn, gives rise to centrifugal forces that deform the molecule away from $D_{3h}(M)$ geometrical symmetry, leading to the formation of a small, non-vanishing dipole moment in the vibrational ground state (see also the prediction of a pure rotational spectrum of H$_2^+$55,56). This explains the form of the rotational band in Fig. 1: the strongest transitions involve the states with the smallest $K$-values. The transitions in the two bands with $K = 0 \leftarrow 3$ and $K = 3 \leftarrow 0$, respectively, have intensities (and Einstein coefficients) about twice as strong as the transitions in the bands involving states with $K \neq 0$ only. Quantum mechanically, this is explained by the special-case nature of the $K = 0$ wavefunctions giving rise to an “extraneous” factor of 2 in the expression for the line strength (see, for example, Eq. (12.33) of Ref. 51). A more detailed analysis of the rotational eigenfunctions obtained at very high $J$-values is presented below in connection with the discussion of the rotational-cluster-formation phenomenon.

IV. A HYBRID, EMPIRICAL-AB INITIO ROTATIONAL LINE LIST FOR $^{32}$S$^{16}$O$_3$

We have previously generated a list of transitions for $^{32}$S$^{16}$O$_3$ which were included in the 2012 edition of the HITRAN database.5 For this we took available experimental transitions2–8 and compared this experimental data to entries in our computed room-temperature line list, adapting the relative intensity measurements to our absolute scale.1 At the same time, we also presented a variationally computed, $ab$ initio line list for $^{32}$S$^{16}$O$_3$. In this list, both the line positions and the transition intensities were obtained variationally with TROVE. However, the line positions of 25 pure rotational transitions were measured by Meyer et al.10 and our HITRAN list included these 25 experimental microwave lines augmented with our theoretical values for the transition intensities. In the present work, we extend our room-temperature line list to include additional rotational transitions. For this we use the ground state rotational constants and centrifugal distortion parameters for $^{32}$S$^{16}$O$_3$ of Makii et al.5 in conjunction with the expression

$$F(J, K) = B_0 J(J + 1) + (C_0 - B_0)K^2 - D_0^J [J(J + 1)]^2$$

$$- D_0^K J(J + 1)K^2 - D_0^K J(J + 1)^3 + H_0^K [J(J + 1)]^2 + H_0^K J(J + 1)K^4 + H_0^K J(J + 1)^2 \pm \delta_{\Delta K} \Delta_0 [J(J + 1)][J(J + 1) - 2][J(J + 1) - 6]$$

(10)

to generate rotational energies for $J$ up to 85. These constants have already been used in the analysis of the spectra presented in Refs. 2–8. To make sure that the extrapolation to high-$J$ states is reasonable, we compare the energy values determined from Eq. (10), and the corresponding transition wavenumbers, with those generated by TROVE. We find a very good agreement, with a root-mean-square difference of only 0.0167 cm$^{-1}$ for all rotational transitions involving states with $K = 0$. The dipole moment vanishes at $D_{3h}(M)$ geometrical symmetry, leading to the formation of a small, non-vanishing dipole moment in the vibrational ground state (see also the prediction of a pure rotational spectrum of H$_2^+$55,56). This explains the form of the rotational band in Fig. 1: the strongest transitions involve the states with the smallest $K$-values. The transitions in the two bands with $K = 0 \leftarrow 3$ and $K = 3 \leftarrow 0$, respectively, have intensities (and Einstein coefficients) about twice as strong as the transitions in the bands involving states with $K \neq 0$ only. Quantum mechanically, this is explained by the special-case nature of the $K = 0$ wavefunctions giving rise to an “extraneous” factor of 2 in the expression for the line strength (see, for example, Eq. (12.33) of Ref. 51). A more detailed analysis of the rotational eigenfunctions obtained at very high $J$-values is presented below in connection with the discussion of the rotational-cluster-formation phenomenon.
Table I. Comparison of rotational term values for $^{32}$S$^{16}$O$_3$ obtained by inserting the experimentally derived, effective rotational constant values from Maki et al.\textsuperscript{5} in Eq. (10) ("Obs.") with theoretical TROVE values from the present work ("Calc.").

<table>
<thead>
<tr>
<th>$J$</th>
<th>$K$</th>
<th>Obs. (cm$^{-1}$)</th>
<th>Calc. (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3</td>
<td>8.885</td>
<td>8.886</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>24.200</td>
<td>24.203</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>38.336</td>
<td>38.342</td>
</tr>
<tr>
<td>20</td>
<td>18</td>
<td>89.825</td>
<td>89.837</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>146.333</td>
<td>146.355</td>
</tr>
<tr>
<td>50</td>
<td>48</td>
<td>486.469</td>
<td>486.514</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>886.775</td>
<td>886.897</td>
</tr>
<tr>
<td>85</td>
<td>84</td>
<td>1315.569</td>
<td>1315.283</td>
</tr>
<tr>
<td>85</td>
<td>3</td>
<td>2529.972</td>
<td>2530.258</td>
</tr>
</tbody>
</table>

$J \leq 85$. Table I shows examples of comparisons between rotational term values in the vibrational ground state of $^{32}$S$^{16}$O$_3$ calculated from Eq. (10) and values obtained variationally with TROVE. The 25 lines from the previous HITRAN-reduced energies constitute a significant extension on the 25 microwave transitions presently included in HITRAN.

V. ROTATIONAL ENERGY CLUSTER FORMATION IN HIGH-J STATES OF SO$_3$

To investigate the possible rotational-energy cluster formation in SO$_3$, we have computed rovibrational term values of $^{32}$S$^{16}$O$_3$ for $J \leq 250$. The present work is focused on rovibrational states in the vibrational ground state, and so the calculation aims at obtaining accurate results for these states only. Because of this, we were able to reduce with impunity the size of the vibrational basis: We employ only basis functions satisfying $P \leq P_{\text{max}} = 8$ (see Sec. II). We denote a rotational term value for SO$_3$ as $E_{J,K}$ and define the reduced energy $\Delta E_{J,K} = E_{J,K} - E_{J,K}^{\text{max}}$, where $E_{J,K}^{\text{max}}$ is the maximum energy found in a given $J$ multiplet of the vibrational ground state (see, for example, Refs. 26, 31, 36, and 37). We visualize the rotational-energy-cluster formation by plotting the reduced energies $\Delta E_{J,K}$ against $J$ in Fig. 3(a) for all states including those forbidden by the nuclear state statistics. The figure shows that for $J > 150$, energy-level clusters form for $^{32}$S$^{16}$O$_3$ in a manner similar to that previously described for the pyramidal molecules PH$_3$, BiH$_3$, and SbH$_3$\textsuperscript{26,31,36,37} at significantly lower $J$ values. The four highest energies in each $J$ manifold cluster together. In conventional symmetric-top notation, these highest four energy levels, taken in descending order, have $K = \kappa = 0, 1, 2, \text{and } 3$, respectively, and the $D_{J_\kappa}(M)$ symmetries $A_1'$, $E''$, $E'$, and $A_2''$ ($A_2'$, $E'$, $E''$, and $A_1''$) for $J$ even (odd). Since the states of $E$ symmetry are doubly degenerate, the four energies define a near-degenerate six-fold cluster. However, for S$^{19}$O$_3$, only one of these four levels is symmetry allowed by the nuclear statistics, see Fig. 3(a), where these levels are indicated with crosses; for other isotopologues, e.g., S$^{18}$O$_3$, all of the levels exist.

Figure 3(b) compares the reduced energy values obtained with TROVE with values determined from Eq. (10), using the experimentally derived values of the required rotation-vibration parameters from Ref. 5. Although the reduced energies obtained from Maki et al. Equation (10) does not exhibit a 6-fold cluster formation at the high $J$ limit, there is a clear tendency in the shape of the $K = 3$ curve to approach the topmost, $K = 0$ energy levels. However, all other rotational states are completely misplaced indicating the deficiency of the simplistic model of Eq. (10) to describe the energy levels with very high $J$. The expansion (10) is truncated after the 6th order terms and we must expect that higher-order terms become important at $J > 150$. In consequence, Eq. (10) is not suitable for extrapolation to states with so high $J$-values, and we take the TROVE results to be more reliable.

A. Origin of the cluster states

It is accepted and has been described in detail\textsuperscript{25} that rotational clustering is associated with symmetry breaking of...
the RES and the corresponding stationary points. For the XY$_3$ type pyramidal molecules the formation of six-fold rotational-energy clusters can be explained in terms of classical arguments that we outline briefly here. In the cluster states, the rotation of XY$_3$ can be thought of as taking place around one of three possible, so-called localization axes, which represent the stationary points, or relative equilibria of the corresponding RES.$^{26, 31, 37}$ For pyramidal XY$_3$ molecules these three symmetrically equivalent axes are of the C$_2$ type and nearly coincide with the three X-H bonds of the XH$_3$ molecule, where H is the proton labelled $i = 1, 2, 3.$$^{31, 37}$ For each of the three localization axes there is the possibility of clockwise or anticlockwise rotation and so six equivalent physical situations emerge, all six having approximately the same energy. The stationary points are the six maxima on the RES, which constitute a six-fold near-degenerate energy cluster. The cluster states are stabilized by large energy barriers separating each of the six equivalent situations just described.

Quantum mechanically of the concept a primitive cluster state (PCS) function is customarily used to describe these situations.$^{30, 32}$ When the PCSs are separated by energy barriers so high as to effectively prevent tunneling between the states, the six equivalent PCS situations become degenerate and the manifold of wavefunctions associated with their common energy can be viewed as a six-dimensional space where the PCS, or coherent wavefunctions, serve as a convenient basis set. Jensen and Kozin$^{30}$ constructed the PCS wavefunctions of an XH$_3$ molecule using the symmetry properties of the corresponding eigenstates. Yurchenko et al.$^{31}$ obtained the PCS wavefunctions for an XH$_3$ molecule by diagonalizing a matrix representing the angular momentum. Below we follow this latter approach in constructing and visualizing the (quantum-mechanical) PCS wavefunctions for SO$_3$, a planar XY$_3$ molecule.

B. Classical analysis in terms of the rotational energy surface

Classically, the rotational cluster formation can be understood in terms of the topology of the rotational energy surface. For a given value of $J$, the RES is obtained as a radial plot of the function $E_J(\theta, \phi)$. This function yields the classical rotational energy in terms of the two angles $(\theta, \phi)$ defining the orientation of the classical angular momentum vector in the molecule-fixed axis system xyz. Thus, the xyz components of the classical angular momentum vector, $(J_x, J_y, J_z)$, are given by according to the relations

$$J_x = \sqrt{J(J+1)} \hbar \sin \theta \cos \phi,$$

$$J_y = \sqrt{J(J+1)} \hbar \sin \theta \sin \phi,$$

$$J_z = \sqrt{J(J+1)} \hbar \cos \theta,$$

where $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi]$. Obviously, in this semi-classical approach we assume the angular momentum vector to have its "quantum-mechanical" length of $\sqrt{J(J+1)} \hbar$

A traditional approach to construct RES is to apply Eqs. (11)–(13) to an effective rotational Hamiltonian.$^{11, 16, 18, 20, 57}$ We follow and alternative, perturbation-theory free approach$^{26, 30, 31}$ and obtain a classical Hamiltonian function $H_n$, by applying the classical limit to the quantum-mechanical Hamiltonian operator $\hat{H}$ (Eq. (5)), i.e., to an "ab initio Hamiltonian" as was proposed by Harter.$^{18}$ Here, $\hat{T}$ is the classical kinetic energy and the momentum $p_n (n=1, 2, \ldots, 6)$ are conjugate to the generalized coordinates $\xi_n$ and $\rho$ described above. The rotational energy surface $E_J(\theta, \phi)$ is then generated on a regular grid of angle points $\theta_m, \phi_m$ by setting the vibrational coordinates in $\hat{H}$ to the optimized geometries $\xi_n^{(opt)}$ and $\rho^{(opt)}$ for each orientation of the angular momentum defined by the polar and azimuthal angles $(\theta_m, \phi_m)$ and Eqs. (11)–(13):

$$E_J(\theta_m, \phi_m) = H_n(J, \xi_n^{(opt)}, \rho^{(opt)}; \theta_m, \phi_m).$$

We also set the generalized vibrational momenta $p_n = \delta T/\delta q_n$ to zero,$^{22}$ which has been shown to be a good approximation.$^{31, 36}$ A more accurate approach$^{26}$ is to include the values of classical $p_n$ into the optimization procedure. Finally, the RES is given by a radial plot of the function

$$E_J^{(RES)}(\theta_m, \phi_m) = E_J(\theta_m, \phi_m) - E_J^{(min)},$$

where $E_J^{(min)}$ is the minimum value of $E_J(\theta_m, \phi_m)$. An example of the RES of SO$_3$, computed for $J = 200$, is shown in Fig. 4. The resulting RES has a doughnut-like shape with six symmetrically equivalent maxima in the $xy$ plane (i.e., for $\theta = 90^\circ$). These maxima are difficult to recognize in Fig. 4 but they are better seen in the top display of Fig. 5, which shows the slice of the RES along a path where $\theta_m$ is kept constant at $90^\circ$ and $\phi_m$ is varied from $0^\circ$–$360^\circ$.

We have already mentioned that when energy clusters form for pyramidal XH$_3$ molecules, the six maxima on the RES corresponding to the top clusters in a $J$ manifold are located in the directions defined by the local C$_2$ symmetry axes associated with the plane containing a X–H molecular bond. For SO$_3$, however, the six maxima appear for $\theta = 90^\circ$ and $\phi = 30^\circ, 90^\circ, 150^\circ, 210^\circ$, and $330^\circ$, respectively, all in the molecular plane. Each of these directions is perpendicular to one of the S–O bonds and also define the orientations of the localization axes A. The molecular geometries corresponding to the maxima on the RES are illustrated by the two lower panels of Fig. 5. For a molecular geometry, associated with the first stationary rotational axis and illustrated in Fig. 6, the localization axis $A = C_z^1$ is perpendicular to the S–O$_1$ bond and the molecular structure has a $C_{2v}$ symmetry with

![FIG. 4. The rotational energy surface of SO$_3$ at $J = 200$.](image-url)
S–O₂ and S–O₃ elongated and the angle \( \alpha_1 = \angle(O_2–S–O_3) \) reduced from 120° to 112.4°. These six maxima are relatively small and separated by less pronounced barriers comparing to the clustering of XH₃ pyramidal molecules. However, their rotational energy-clustering structure (see Fig. 3) is very similar, despite these differences in the topology of the RESs of a planar SO₃ molecule from that encountered for pyramidal XY₃ molecules.

C. Quantum-mechanical analysis

We supplement the classical RES analysis of the cluster-formation phenomenon by a determination of the quantum-mechanical PCS wavefunctions; these wavefunctions are obtained using a technique already described elsewhere. For a given \( J \)-value, we solve the Schrödinger equation for the Hamiltonian in Eq. (5) using TROVE. That is, we initially diagonalize the Hamiltonian matrix blocks for all \( D_{3h}(M) \) symmetries, using the basis set defined by \( P_{\text{max}} = 8 \). We then select the six near-degenerate eigenfunctions \( \psi_n^{(J)} \) associated with the “top” cluster in the appropriate \( J \) manifold of the vibrational ground state, and search for six localization directions \( A_i \) and associated PCS \( \psi_n^{(J)} \) such that the molecule has the largest possible absolute value of the angular momentum projection, \( J \cdot h \), onto the localization axis \( A_i \) associated with \( \psi_n^{(J)} \). This procedure is justified when the six states \( \psi_n^{(J)} \) are so close to being degenerate that any linear combination of them can be taken to be an eigenfunction of the rovibrational Hamiltonian. For example, in the two states \( |1 \text{ PCS} \rangle \) and \( |2 \text{ PCS} \rangle \), the molecule has angular momentum projections of \( +m \hbar \) and \( -m \hbar \), respectively, with \( m \approx J \), onto the localization axis \( A_1 \). In the case of SO₃ we know that the localization axes are in the molecular plane (\( \theta_A = 90^\circ \)) and only the azimuthal angle \( \phi_4 \) must be determined.

In agreement with the classical results, the localization axes are found to be perpendicular to one of the S–O bonds, that is, with \( \phi_4 = 30^\circ, 90^\circ, 150^\circ, 210^\circ, 270^\circ, \) or \( 330^\circ \). It should be noted that the PCS functions associated with these directions could also be obtained from the six eigenfunctions \( \psi_n^{(J)} \) based solely on their symmetries, see, for example, Ref. 30.

We visualize the PCS states by plotting their reduced rotational densities, obtained by integrating the square of the corresponding wavefunction \( |n \text{ PCS} \rangle \) over all vibrational coordinates and over the Euler angle \( \alpha \):

\[
F(\beta, \gamma) = \int_0^{2\pi} d\alpha \int_{\text{vib}} dV \left( \psi_n^{\text{PCS}} \right)^* \psi_n^{\text{PCS}},
\]

where \( \psi_n^{\text{PCS}} = |n \text{ PCS} \rangle \) and \( dV \) is the volume element associated with the vibrational coordinates. We use the explicit form of the rotational functions \( D_{J, K \cdot m}(\alpha, \beta, \gamma) \)⁵⁰ for \( m = J \) so that the molecule is aligned with the angular momentum oriented along the space fixed Z axis to the greatest extent allowed by quantum mechanics (see Ref. 31 for details). The Euler angles \( \beta, \gamma \) define the orientation of the space-fixed Z axis relative to the molecule-fixed axis system \( xyz \). Examples of probability distributions \( F(\beta, \gamma) \) obtained for \( \psi = |1 \text{ PCS} \rangle \) at \( J = 100, 150, 200, \) and 250 are shown in Fig. 7 (Multimedia view), where the \( F(\beta, \gamma) \) functions are imaged onto Bloch spheres of arbitrary radii. The maxima of the \( F(\beta, \gamma) \) distributions indicate how the molecule prefers to align itself relative to the space-fixed Z axis and, since \( m = J \), to the angular momentum vector which we can think of as being classical in these highly excited rotational states. The classical angular momentum vector is conserved in space and time so that it defines the axis of rotation. The vibrationally averaged structure, the molecule-fixed axis system \( xyz \), and the localization axis \( A \) are indicated for the \( |1 \text{ PCS} \rangle \) state in Fig. 6. We illustrate how cluster states differ from non-cluster states in Fig. 8 (Multimedia view) which represents the probability distributions \( F(\beta, \gamma) \) for the states with \( (J, K) = (100, 99) \) and \( (100, 96) \), respectively. In these states, the rotation obviously takes place around the \( z \) axis which is perpendicular to the molecular plane and the angular momentum precesses about this axis.

In the two panels of Fig. 8 (Multimedia view), the precessing angular momentum forms angles of roughly 9° and 18°, respectively, with the \( z \) axis. The angles associated with these precessions compare well with the classical interpretation of the orientation of the rotation axis relative to the \( z \) axis defined.
VI. SUMMARY AND CONCLUSION

As part of the present work we have generated a “hybrid” line list for $^{32}$S$^{16}$O$_3$, consisting of 3 414 rotational transitions in the vibrational ground state. The transitions take place between rotational states with $J$-values in the range from 0 to 85. The frequencies of the 3 414 rotational transitions are obtained using the “Watsonian” expression of Eq. (10) with the values of the $^{32}$S$^{16}$O$_3$ ground state rotational constants obtained by Maki et al. by least-squares fits to their observed infrared frequencies. The line list values for the intensities of the rotational transitions are purely theoretical. They are computed with the TROVE program from ab initio potential energy and dipole moment surfaces reported previously.1 We suggest that the new line list data be included in the HITRAN database since, at present, the only SO$_3$ information available there comprises 25 experimentally measured line frequencies for rotational transitions of $^{32}$S$^{16}$O$_3$. The new theoretical data from the present work are given as the supplementary material and also available at www.exomol.com as a part of the ExoMol project.

Furthermore, we have investigated in the present work by theoretical methods the formation of near-degenerate rotation-vibration energy clusters in the vibrational ground state of $^{32}$S$^{16}$O$_3$ at high rotational excitation. We report here for the first time theoretical predictions of such cluster states for an XY$_3$ molecule that is planar at equilibrium. Using variational nuclear motion calculations we predict the formation of six-fold near-degenerate energy-level clusters in the vibrational ground state of $^{32}$S$^{16}$O$_3$ in the $J$ range between 100 and 250. The structure of the rotational energy clusters is similar to that previously described for the pyramidal XH$_3$ molecules. However the cluster-formation mechanism is different: Whereas in the pyramidal molecules the rotation in the cluster states can be thought of as taking place around so-called stabilization axes roughly coinciding with the X–H bonds, for SO$_3$ each stabilization axis is perpendicular to one of the S–O bonds, see Fig. 6. In the cluster states at $J \geq 100$, the bond perpendicular to the stable rotational axis is significantly elongated by centrifugal forces. Since the two other bonds are not orthogonal to the axis of rotation, they are less elongated, but the angle $\alpha_1$ between them is decreased by the centrifugal distortion (Fig. 6).

The rotational-energy clustering of SO$_3$ is special because of the small rotational constants. Since the rotational clustering of heavy molecules, such as CF$_4$ and SF$_6$, has been successfully studied experimentally, we hope that our results will encourage experimentalists to confirm the existing stabilization rotations for SO$_3$ as well. Indeed highly excited rotational levels of SO$_3$ should be present and observable at temperatures about 800 K using recently proposed techniques.60

We note once again that for the $^{34}$O$_3$ isotopologue, the clusters are hypothetical since in this case, the nuclear statistics permits only rotation-vibration states of $A_1^3$ and $A_2^1$ symmetry and so in reality, each six-fold cluster will comprise a single existing energy level accompanied by three “missing levels.” For isotopologues containing oxygen isotopes with non-zero spin such as $^{18}$O$_3$, however, all cluster components will exist.
Apart from high-\(T\) conventional spectroscopy, another possibility of populating highly excited rotational states experimentally is by the optical-centrifuge technique pioneered by Karczmarek et al.\(^{15}\) In Ref. 61, it was speculated for other molecules with energy clusters that states with PCS properties could be prepared by means of optical-centrifuge techniques. These states are given as superpositions of near-degenerate energy eigenstates and would therefore be long-lived. In consequence, it may be possible to verify their existence experimentally. Again, the formation of the PCS-like states cannot take place for \(\text{SO}_3\) since the required near-degenerate eigenstates are missing, but for \(\text{S}^{18}\text{O}_3\) such experiments could be feasible.

Finally we note that a hot \(\text{SO}_3\) line list is under construction as part of ExoMol project.\(^{59}\) Results of these calculations will be reported elsewhere.\(^{62}\)

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52 See supplementary material at http://dx.doi.org/10.1063/1.4882865 for a HITRAN-style line list of pure rotational transitions.