

## Effect of kinetic energy terms on the vibrational frequencies ( $\nu_1, \nu_3$ ) in the ${}^1B_2$ ( ${}^1A'$ ) excited state of $\text{SO}_2$

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**Abstract.** The effect of various kinetic energy terms on the solution of the two-dimensional Schrödinger equation; involving the two large-amplitude stretching modes  $\nu_1$  and  $\nu_3$  of  $\text{SO}_2$  in its  ${}^1B_2$  excited state, is discussed. Employing two large amplitude Hamiltonian  $H_s^0(\rho_1, \rho_3)$  obtained earlier, three sets of force constants were obtained. In obtaining set 1, all the 6 coefficients of the kinetic energy  $A, H, B, G, F,$  and  $C$  were taken into account and varied with  $(\rho_1, \rho_3)$ . For set 2, only the three coefficients  $A, H,$  and  $B$ , evaluated at the absolute minima  $(\rho_1^e + \delta, \pm \rho_3^e)$  were considered. In obtaining the set 3 constants, only the two coefficients  $A$  and  $B$  evaluated at the saddle point  $(\rho_1^e, 0)$  were retained. The nine force constants of the potential  $V_0(\rho_1, \rho_3)$  which includes a double minimum function in  $\rho_3$ , were obtained in each case by a least squares fit to the 12 vibrational frequencies corresponding to the levels  $(\nu_1, \nu_3) = (0, 2), (1, 0), (1, 2), (2, 0), (0, 6)$  and  $(3, 0)$  of  $\text{S}^{16}\text{O}_2$  and  $\text{S}^{18}\text{O}_2$ . It is found that set 2 is superior to set 3, and sets 1 and 2 fit the frequencies essentially to the same degree of accuracy.

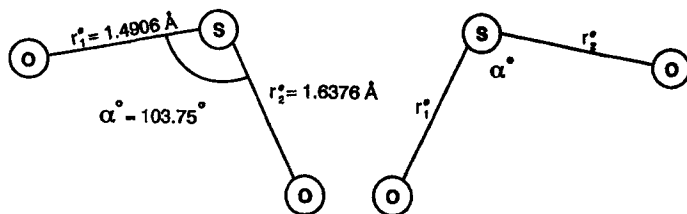
**Keywords.** Two-dimensional Schrödinger equation; excited states of  $\text{SO}_2$ ; vibrational frequencies.

### 1. Introduction

It is reasonably well established (Brand and Rao 1976; Hoy and Brand 1978; Mezey and Rao 1980) that the  ${}^1B_2$  state of the  $\text{SO}_2$  molecule has an unsymmetrical equilibrium structure corresponding to a double minimum potential in the antisymmetrical strength coordinate  $\rho_3$  (see figure 1). A two-dimensional model for the Hamiltonian with a potential  $V(q_1, q_3)$  was developed (Hoy and Brand 1978) and used successfully to explain a group of observed quantities including vibrational term values of  $\text{S}^{16}\text{O}_2$  and  $\text{S}^{18}\text{O}_2$ . Subsequently, the vibrational frequencies of  $\text{S}^{16}\text{O}_2$  and  $\text{S}^{18}\text{O}_2$  were calculated (Mezey and Rao 1980) by solving a more rigorous two-large amplitude equation obtained earlier (Brand and Rao 1976). This two-large amplitude Hamiltonian  $H_s^0(\rho_1, \rho_3)$  contains a potential  $V_0(\rho_1, \rho_3)$  which not only has fewer parameters than the observed vibrational term values but is more nearly isotopic invariant than any other model potential considered before.

In the two large-amplitude formalism (Brand and Rao 1976), the kinetic energy expression has six terms with coefficients  $A, H, B, G, F,$  and  $C$  which are functions of  $\rho_1$  and  $\rho_3$ . The potential energy  $V^0(\rho_1, \rho_3)$  is taken to contain nine constants.

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**Figure 1.** Unsymmetrical equilibrium structure of  $\text{SO}_2$  in its  ${}^1B_2({}^1A')$  excited state.  $2\rho_1 = r_1 + r_2$ ,  $2\rho_3 = r_1 - r_2$  and  $\alpha^\circ$  is fixed at  $103.75^\circ$ .

The corresponding Schrödinger equation is an elliptic eigenvalue partial differential equation in two variables  $\rho_1$  and  $\rho_3$  satisfying the constraint

$$H^2 - AB < 0.$$

In the present state of the art, all the three vibrations of a nonlinear triatomic molecule are dealt with rigorously and with high accuracy using a variety of techniques (Choi and Light 1992; Jensen and Kozin 1993; Polyansky *et al* 1993). In particular, Handy and coworkers (Handy 1987; Bramley *et al* 1991; Whitehead and Handy 1995) have treated the three vibrations of a triatomic molecule rigorously with an exact expression for the kinetic energy operator. Such an exact treatment becomes relevant if the complete potential for the 3 modes is deduced from experiment or is constructed from *ab initio* computation of electronic energy.

In the present communication, we consider only  $(\nu_1, \nu_3)$  frequencies of the excited state as data are available only for these frequencies. We will study the effect of various terms of the kinetic energy on the vibrational frequencies  $(\nu_1, \nu_3)$  of  $\text{SO}_2$ . We obtained three sets of force fields (set 1, set 2 and set 3) each fitted to 12 frequencies of  $\text{S}^{16}\text{O}_2$  and  $\text{S}^{18}\text{O}_2$ . In obtaining set 1, all the six terms of the kinetic energy were retained and varied with  $(\rho_1, \rho_3)$  and the nine potential constants were refined to fit the 12 frequencies. For set 2, only terms with coefficients  $A$ ,  $H$ , and  $B$  of the kinetic energy, evaluated at the absolute minima, were retained and the force field refined. Set 3 is the more traditional one (Carreira *et al* 1972; Hoy and Brand 1978; Wilson *et al* 1980) and its kinetic energy has terms with coefficients  $A$  and  $B$  evaluated at the saddle point.

## 2. The Hamiltonian

The two large-amplitude zeroth order Hamiltonian describing the two stretching motions  $\rho_1$  and  $\rho_3$  of any bent triatomic molecule with masses  $m_1, m_2$  and  $m_3$  is given by (Brand and Rao 1976; Mezey and Rao 1980),

$$H_s^0(\rho_1, \rho_3) = \frac{-h^2}{2\Delta_{13}^0} \left( I_{33}^0 \frac{\partial^2}{\partial \rho_1^2} - 2I_{13}^0 \frac{\partial^2}{\partial \rho_1 \partial \rho_3} + I_{11}^0 \frac{\partial^2}{\partial \rho_3^2} + 2G \frac{\partial}{\partial \rho_1} + 2F \frac{\partial}{\partial \rho_3} + C \right) + V_0(\rho_1, \rho_3). \quad (1)$$

Here  $\rho_1$  and  $\rho_3$  describe the two stretching motions given by

$$2\rho_1 = r_1 + r_2, \quad 2\rho_3 = r_1 - r_2 \quad (2)$$

where  $r_1$  and  $r_2$  are the instantaneous values of the bond lengths of the reference configuration (Brand and Rao 1976, figure 1). In what follows, we shall omit, for

brevity, the superscript 0 for the quantities in (1) denoting zeroth order. The coefficients  $A = I_{11}$ ,  $H = -I_{13}$ ,  $B = I_{33}$ ,  $G$ ,  $F$  and  $C$  in (1) are functions of  $\rho_1$  and  $\rho_3$ . They are given by (35) (Brand and Rao 1976). The value of  $\Delta_{13}$  is given by

$$\begin{aligned}\Delta_{13} &= I_{11}I_{33} - (I_{13})^2 \\ &= 4m_1m_2m_3/M.\end{aligned}\quad (3)$$

The units of  $H_s$  are ergs when  $\rho_1$  and  $\rho_3$  are expressed in Å,  $I_{11}$ ,  $I_{13}$  and  $I_{33}$  in amu,  $\Delta_{13}$  in (amu)<sup>2</sup>,  $G$  and  $F$  in (ergs. Å),  $C$  and  $V_0$  in ergs.  $H_s/hc$  is in  $\text{cm}^{-1}$ .

The potential function  $V_0(\rho_1, \rho_3)$  is given by

$$\begin{aligned}V_0(\rho_1, \rho_3) &= \frac{1}{2}K_{11}(\rho_1 - \rho_1^e)^2 + \frac{1}{2}K_{111}(\rho_1 - \rho_1^e)^3 + \frac{1}{24}K_{1111}(\rho_1 - \rho_1^e)^4 \\ &\quad + \frac{1}{2}K_{33}\rho_3^2 + k_1e^{-k_2\rho_3^2} + \frac{1}{24}K_{3333}\rho_3^4 + \frac{1}{2}K_{133}(\rho_1 - \rho_1^e)\rho_3^2 \\ &\quad + \frac{1}{4}K_{1133}(\rho_1 - \rho_1^e)^2\rho_3^2.\end{aligned}\quad (4)$$

Here  $V_0$  is expanded at the saddle point  $S(\rho_1 = \rho_1^e, \rho_3 = 0)$ , and the absolute minima  $M_1$   $M_2$  are assumed to occur at  $(\rho_1 = \rho_1^e + \delta, \rho_3 = \pm \rho_3^e)$  where  $\delta$  is a small positive number. The constants  $\rho_1^e$  and  $\rho_3^e$  are equilibrium values. The method of finding  $\delta$  as well as the extremal points (critical points) for the potential  $V_0(\rho_1, \rho_3)$  is explained in appendix A of Mezey and Rao (1980). The quadratic and Gaussian terms in  $\rho_3$  of (4) give a double minimum potential in  $\rho_3$ . Even though the complete vibrational problem of a triatomic molecule requires the inclusion of bending angle also, it is not taken into account here as there are no observed values corresponding to levels  $(v_1v_2v_3)$ . The treatment of the vibrational problem given here is inadequate to that extent.

For computational convenience, the Hamiltonian (1) is transformed into dimensionless coordinates  $q_1$  and  $q_3$  given by

$$\begin{aligned}q_1 &= (\gamma_1 I_{11})^{1/2}(\rho_1 - \rho_1^e), \\ q_3 &= (\gamma_3 I_{33})^{1/2}\rho_3,\end{aligned}\quad (5)$$

where

$$\gamma_i = 4\pi^2 c\omega_i/h \quad (i = 1, 3). \quad (6)$$

The values  $\gamma_i$  (ergs<sup>-1</sup> s<sup>-2</sup>) are the scaling factors, and  $I_{11}$  and  $I_{33}$  are the "reduced masses", both being functions of  $(\rho_1, \rho_3)$ . Harmonic frequencies  $\omega_1$  and  $\omega_3$  of (6) are obtained from the harmonic force constants  $K_{11}$  and  $K_{33}$  using the formula

$$\omega_i^2 = K_{ii}/4\pi^2 c^2 I_{ii} \quad (i = 1, 3). \quad (7)$$

When the coefficients of the kinetic energy terms are evaluated at a fixed point (saddle point or absolute minimum), coefficients  $G$ ,  $F$  and  $C$ , being essentially partial derivatives of constants  $I_{\alpha\beta}(\alpha, \beta = x, y, z, 1, 3)$  (Brand and Rao 1976), vanish.

Thus the Hamiltonian, in terms of  $q_1$  and  $q_3$  and the conjugate momenta

$$p_1 = -i \frac{\partial}{\partial q_1} \text{ and } p_3 = -i \frac{\partial}{\partial q_3},$$

becomes

$$H_s(q_1, q_3) = \frac{1}{2}(ap_1^2 + 2hp_1p_3 + bp_3^2) + V_0(q_1, q_3), \quad (8)$$

where

$$a = I_{11} I_{33} \omega_1 / \Delta_{13},$$

$$h = (-I_{13} / \Delta_{13})(I_{11} I_{33} \omega_1 \omega_3)^{1/2} \tag{9}$$

and

$$b = I_{11} I_{13} \omega_3 / \Delta_{13}.$$

The values  $a, h$  and  $b$  of (8) are evaluated at absolute minima  $(\rho_1^e + \delta, \pm \rho_3^e)$ . When they are evaluated at the saddle point  $(\rho_1^e, 0)$ ,  $I_{13} = 0$  and (8) reduces to the traditional Hamiltonian (Carreira *et al* 1972; Hoy and Brand 1978; Wilson *et al* 1980) for two vibrations,

$$H_s(q_1, q_3) = \frac{1}{2}(\omega_1 p_1^2 + \omega_3 p_3^2) + V_0(q_1, q_3). \tag{10}$$

The potential  $V_0(q_1, q_3)$  (in  $\text{cm}^{-1}$ ) in these two cases is given by (Hoy and Brand 1978; Coon *et al* 1966)

$$V_0(q_1, q_3) = \frac{1}{2} \omega_1 q_1^2 + \frac{1}{6} \phi_{111} q_1^3 + \frac{1}{24} \phi_{1111} q_1^4 + \frac{1}{2} \omega_3 q_3^2 + f_1 e^{-f_2 q_3^2}$$

$$+ \frac{1}{24} \phi_{1111} q_1^4 + \frac{1}{2} \phi_{133} q_1 q_3^2 + \frac{1}{4} \phi_{1133} q_1^2 q_3^2, \tag{11}$$

where  $f_1 = B\omega_3 e^\rho / D, f_2 = D/2B$  and  $D = e^\rho - \rho - 1$ .

The nine force constants of  $V_0$  resulting from (8) and (10) are termed set 2 and set 3.  $B\omega_3$  is the barrier height and  $\rho$  is the shape parameter of the double minimum potential  $V(q_3)$  in  $q_3$ . These parameters were originally introduced by Coon *et al* (1966) and subsequently used by Hoy and Brand (1978). The maximum of the one-dimensional potential,

$$V(q_3) = \frac{1}{2} \omega_3 q_3^2 + f_1 e^{-f_2 q_3^2}, \tag{12}$$

occurs at  $q_3 = 0$  and the minima occur at

$$q_3 = \pm [\ln(2f_1 f_2 / \omega_3) / f_2]^{1/2} = \pm q_3^M. \tag{13}$$

giving the barrier height (in  $\text{cm}^{-1}$ ),

$$V^+ - V^- = V(q_3 = 0) - V(q_3 = \pm q_3^M) = B\omega_3. \tag{14}$$

But the barrier height of the two-dimensional potential  $V_0(q_1, q_3)$  is given by the height of the saddle point above the absolute minima (Hoy and Brand 1978; Mezey and Rao 1980),

$$\text{Barrier height} = V_0(\rho_1^e, 0) - V_0(\rho_1^e + \delta, \pm \rho_3^e). \tag{15}$$

### 3. Computational procedure

A variational technique (Brand and Rao 1976; Mezey and Rao 1980; Polyansky *et al* 1993) has been employed to obtain the energy levels  $G(v_1, v_3^{\text{even}})$ , where  $v_1$  and  $v_3$  are

quantum numbers corresponding to the two stretching modes  $\nu_1$  and  $\nu_3$ . We have employed 200 basis functions, 100 functions for  $|v_1, v_3^{\text{even}}\rangle$  and 100 functions for  $|v_1, v_3^{\text{odd}}\rangle$ . For the complete Hamiltonian (1), all the 200 functions have to be employed in obtaining the energy levels, since there are contributions to  $\langle v_1' v_3^{\text{even}} | H_s | v_1 v_3^{\text{even}} \rangle$  coming from terms with coefficients  $H$  and  $F^2$ . For all other terms, there is no mixing of the functions  $|v_1 v_3^{\text{even}}\rangle$  and  $|v_1 v_3^{\text{odd}}\rangle$  to obtain  $(v_1, v_3^{\text{even}})$  levels. For the Hamiltonian (8) or (10), it is enough to use the basis set  $|v_1, v_3^{\text{even}}\rangle$  with even  $v_3$  as we are only interested in obtaining levels with even  $v_3$  in this work.

Three sets of force constants were obtained. In obtaining set 1, all the 6 terms of the kinetic energy with coefficients  $A, H, B, G, F$  and  $C$  were taken into account. These are functions of  $(\rho_1, \rho_3)$  and their matrix elements were evaluated using the Gauss-Hermite quadrature formula (Carnahan *et al* 1969; Press *et al* 1989). We have used 20 zeros of the Hermite polynomial  $H_{20}(q) = 0$  and the corresponding weight functions to evaluate the integrals of these functions. The complete  $(100 \times 100)$  matrix of the Hamiltonian  $\langle v_1' v_3^{\text{even}} | H_s | v_1 v_3^{\text{even}} \rangle$  with 15 terms (6 kinetic energy and 9 potential energy terms) was then diagonalized to obtain the energy levels  $G(v_1, v_3^{\text{even}})$ .

In set 2, the six coefficients of the kinetic energy were fixed at the absolute minima  $(\rho_1^e + \delta, \pm \rho_3^e)$ . This eliminates terms with coefficients  $G, F$  and  $C$  and we are left with the Hamiltonian (8). In set 3, the coefficients were evaluated at the saddle point  $(\rho_1^e, 0)$  and the resulting Hamiltonian (10) contains only two kinetic energy terms. This is the conventional Hamiltonian used for a 2-dimensional vibrational problem (Hoy and Brand 1978; Handy 1987; Bramley *et al* 1991).

#### 4. Adjustment of force constants

$\rho_1^e$  and  $\alpha^0$  (the bond angle) were fixed at 1.5525 Å and  $103.75^\circ$  respectively (Hoy and Brand 1978; Mezey and Rao 1980). The initial set of nine force constants  $K_{11}, K_{111}, K_{1111}, K_{33}, k_1, k_2, K_{3333}, K_{133}$  and  $K_{1133}$  were obtained (Mezey and Rao 1980) where they were refined to fit the 12 vibrational frequencies corresponding to the levels  $(v_1, v_3) = (0, 2), (1, 0), (1, 2), (2, 0), (0, 6)$  and  $(3, 0)$  of  $S^{16}O_2$  and  $S^{18}O_2$ . Unlike in Mezey and Rao (1980), the potential is here expanded at  $(\rho_1 - \rho_1^e, 0)$  and hence the geometry is slightly different.

All computations were carried out using a VAX 4000/200 computer. It required approximately 10 minutes to compute the 12 frequencies of  $S^{16}O_2$  and  $S^{18}O_2$  for set 1, and 2 minutes each for sets 2 and 3. It was not always easy to do a least squares calculation using normal equations for the adjustment of force constants. Therefore, we have used method D (Shimanouchi and Suzuki 1965; Ueda and Shimanouchi 1967) which circumvents the inversion of an ill-conditioned normal matrix even though it does not remove the inherent problems associated with it. In their method D, each force constant is adjusted in succession by a certain factor  $\lambda$  so that the sum of the squared deviations between the observed and calculated frequencies becomes smaller with each successive iteration. When this no longer happens, a new  $\lambda$  is obtained by multiplying it with  $\mu$  ( $0 < \mu < 1$ ) and the computations are continued. The adjustment procedure is terminated when  $\lambda$  by successive multiplications with  $\mu$  ( $\lambda, \mu\lambda, \mu^2\lambda, \dots$ ) becomes so small that the change of the force constants by  $\lambda$  no longer affects the sum of squared deviations [SES - squared error sum:  $\sum_i^{12} (v_{\text{obs}} - v_{\text{cal}}^i)^2$ ].

**Table 1.** Kinetic energy coefficients ( $I_{11}$ ,  $I_{13}$ ,  $I_{33}$ ) and force constants of  $\text{SO}_2$  in large amplitude coordinates ( $\rho_1, \rho_3$ )<sup>a</sup>. See (4) for  $V_0(\rho_1, \rho_3)$ .

Force constants	Set 1	Set 2		Set 3	
		$\text{S}^{16}\text{O}_2$	$\text{S}^{18}\text{O}_2$	$\text{S}^{16}\text{O}_2$	$\text{S}^{18}\text{O}_2$
$I_{11}(\text{amu})$		25·894810	28·734259	25·899934	28·740817
$I_{13}(\text{amu})$		0·109044	0·139562	0·0	0·0
$I_{33}(\text{amu})$		19·781843	21·245190	19·777470	21·239664
$K_{11}(\text{mdyn}/\text{\AA})$	13·41405		13·405051		13·474051
$K_{111}(\text{mdyn}/\text{\AA}^2)$	-124·49120		-123·751198		-123·751198
$K_{1111}(\text{mdyn}/\text{\AA}^3)$	329·01305		318·013051		321·563051
$K_{33}(\text{mdyn}/\text{\AA})$	4·48724		4·479237		4·495237
$K_{3333}(\text{mdyn}/\text{\AA}^3)$	306·14337		305·093372		304·643372
$k_1(\text{mdyn}\cdot\text{\AA})$	0·03766		0·037555		0·037655
$k_2(\text{\AA}^{-2})$	88·43281		87·582814		88·412814
$K_{133}(\text{mdyn}/\text{\AA}^2)$	-58·88147		-58·941471		-59·036471
$K_{1133}(\text{mdyn}/\text{\AA}^3)$	384·56279		384·112786		377·562790

<sup>a</sup>Set 2 constants were obtained at absolute minima ( $\rho_1^e + \delta, \pm \rho_3^e$ ), and set 3 constants at saddle point ( $\rho_1^e, 0$ )

**Table 2.** Kinetic energy coefficients ( $a, h, b$ ) and force constants (in  $\text{cm}^{-1}$ ) of  $\text{SO}_2$  in dimensionless coordinates ( $q_1, q_3$ )<sup>a</sup>. See (11) for  $V_0(q_1, q_3)$ .

Parameters	Set 2		Set 3	
	$\text{S}^{16}\text{O}_2$	$\text{S}^{18}\text{O}_2$	$\text{S}^{16}\text{O}_2$	$\text{S}^{18}\text{O}_2$
$a$	937·40	889·89	939·70	892·04
$h$	-3·6722	-4·1206	0·0	0·0
$b$	619·95	598·22	621·13	599·35
$\omega_1$	937·36	889·86	939·70	892·04
$\phi_{111}$	-322·50	-298·30	-321·16	-297·10
$\phi_{1111}$	30·8874	27·8352	31·0661	27·9954
$\omega_3$	619·94	598·20	621·13	599·35
$\phi_{3333}$	116·0822	108·0862	115·5239	107·5706
$f_1$	1890·70	1890·72	1895·73	1895·73
$f_2$	0·2408	0·2323	0·2426	0·2341
$\phi_{133}$	-304·0255	-285·8350	-303·6017	-285·4400
$\phi_{1133}$	73·8403	67·6398	72·2669	66·1988

<sup>a</sup>In set 1, all the six kinetic energy terms were varied with respect to ( $\rho_1, \rho_3$ ) and hence are not included here; set 2 constants were evaluated at absolute minima ( $\rho_1^e + \delta, \pm \rho_3^e$ ) and set 3 constants at saddle point ( $\rho_3^e, 0$ );

<sup>b</sup> $f_2$  is dimensionless.

## 5. Results and discussion

The kinetic energy coefficients for sets 2 and 3 and force constants for all the three sets are given in table 1. Corresponding values in  $\text{cm}^{-1}$  for sets 2 and 3 are given in table 2. The two tables do not show kinetic energy coefficients for set 1 as they were varied with

( $\rho_1, \rho_3$ ). As mentioned before, all the kinetic energy coefficients were computed at 20 points corresponding to 20 zeros of the Hermite polynomials in the Gauss-Hermite quadrature procedure (Coon *et al* 1966; Carreira *et al* 1972). The values of table 2 correspond to (8) and (10). Observed and difference frequencies for both  $S^{16}O_2$  and  $S^{18}O_2$  for the three sets of constants are given in table 3. Also included in the table are the SES values for the three sets giving the sum of the squared deviations between observed and calculated frequencies. Set 2, which takes into account three kinetic energy terms  $I_{11}$ ,  $I_{13}$  and  $I_{33}$ , is superior to set 3 which employs the conventional expression for the kinetic energy. Barring any unforeseen numerical errors in the lengthy computation, it is somewhat disappointing that set 1, which is the result of a rigorous treatment of kinetic energy, is only as good as set 2. It is hoped that for some other molecules, set 1 will turn out to be superior to sets 2 and 3.

The deviations between observed and calculated values for  $S^{16}O_2$  are in the opposite direction to  $S^{18}O_2$ , indicating the correctness of the calculation (Shimanouchi and Suzuki 1965)\*. There are no significant differences among the three sets of force constants given in table 1 or table 2 as the starting set is very close to the final set. The sum of the squared deviations for the 12 frequencies is  $382.09 \text{ cm}^{-2}$  for set 2 and  $408.86 \text{ cm}^{-2}$  for set 3. This difference amounts to an improvement of  $[(408.86 - 382.09)/12]^{1/2} \sim 1.5 \text{ cm}^{-1}$ , on the average, for each one of the 12 frequencies. In set 2 of table 2, the small differences between  $a$  and  $\omega_1$  on the one hand, and  $b$  and  $\omega_3$  on the other are due to the fact that  $I_{13} \neq 0$  for this set (see (9)).

Table 4 contains the structural parameters and various vibrational constants obtained with set 2 constants. The saddle point and potential minima occur at  $(\rho_1^e, 0)$  and  $(\rho_1^e + \delta, \pm \rho_3^e)$ , where  $\rho_1^e = 1.5525 \text{ \AA}$  and  $\delta = 0.0116 \text{ \AA}$ . The value of  $\delta$  was obtained from the nine force constants of set 2 using the equations given in the appendix of Mezey and Rao (1980). The equilibrium bond lengths are calculated to be

**Table 3.** Observed and difference frequencies (obs-calc) (in  $\text{cm}^{-1}$ ) for the 3 sets of constants<sup>a</sup>.

$(v_1, v_3)$	$S^{16}O_2$				$S^{18}O_2$			
	Obs <sup>b</sup>	Obs-Calc.			Obs <sup>b</sup>	Obs-Calc.		
		Set 1	Set 2	Set 3		Set 1	Set 2	Set 3
(0, 2)	561.30	-0.83	-0.83	-1.14	533.30	0.60	0.52	0.19
(1, 0)	960.30	-5.21	-2.95	-6.82	920.90	2.39	4.85	1.14
(1, 2)	1655.70	0.16	1.39	0.80	1582.30	6.01	7.10	7.09
(2, 0)	1918.10	-4.28	-4.68	-6.31	1840.00	10.55	9.76	9.17
(0, 6)	1965.90	-6.04	-5.94	-7.21	1880.20	6.53	6.41	4.65
(3, 0)	2921.20	-9.34	-9.58	-6.96	2798.40	4.03	3.36	7.93

Squared error sum for 12 frequencies ( $\text{cm}^{-2}$ ): 382.13 for set 1; 382.09 for set 2; 408.86 for set 3.

<sup>a</sup> See table 1; <sup>b</sup> See Hoy and Brand (1978).

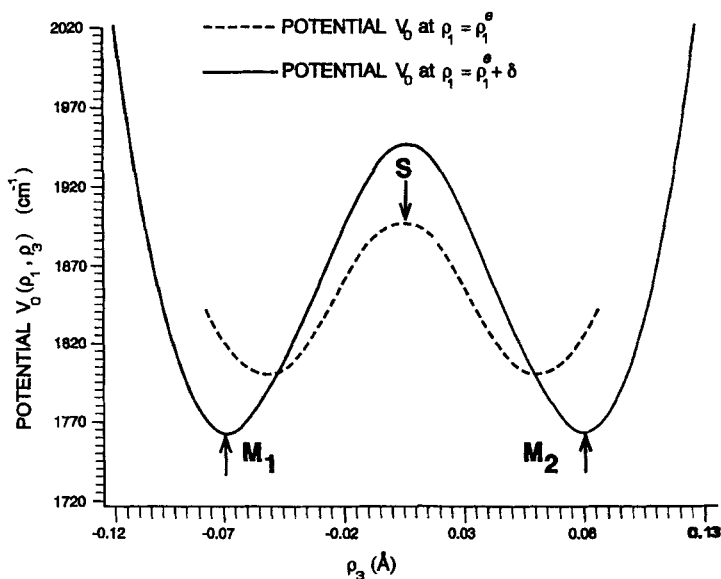
<sup>+</sup> For HCl and DCl molecules with reduced masses  $\mu_{\text{HCl}} = 0.979593 \text{ amu}$  and  $\mu_{\text{DCl}} = 1.904322 \text{ amu}$  and harmonic force constants  $K_{\text{HCl}} = 5.1574 \text{ mdyn/\AA}$  and  $K_{\text{DCl}} = 4.9043 \text{ mdyn/\AA}$ , the harmonic frequencies  $2989 \text{ cm}^{-1}$  and  $2090 \text{ cm}^{-1}$  are fitted exactly. But with  $K = (K_{\text{HCl}} + K_{\text{DCl}})/2$ , the deviations between observed and calculated values are  $+37 \text{ cm}^{-1}$  for HCl and  $-27 \text{ cm}^{-1}$  for DCl.

**Table 4.** Various vibrational constants obtained with set 2 force constants.

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$\rho_1^e = 1.5525 \text{ \AA}$ , $\rho_3^e = \pm 0.0735 \text{ \AA}$ , $\alpha^e = 103.75^\circ$
$\delta = 0.0116 \text{ \AA}$
Saddle point (S) = $(\rho_1^e, 0)$ = $(1.5525, 0) \text{ \AA}$
Absolute minima ( $M_1, M_2$ ) = $(\rho_1^e + \delta, \pm \rho_3^e) = (1.5641, \pm 0.0735) \text{ \AA}$
$V_0$ at S = $1,890.70 \text{ cm}^{-1}$
$V_0$ at $M_1, M_2$ = $1,760.16 \text{ cm}^{-1}$
Barrier height = $(1890.70 - 1760.16) = 130.54 \text{ cm}^{-1}$
Zero point energy $G(0,0)$ = $618.47 \text{ cm}^{-1}$ for $\text{S}^{16}\text{O}_2$
= $590.54 \text{ cm}^{-1}$ for $\text{S}^{18}\text{O}_2$
Isotopic shift = $-20.81 \text{ cm}^{-1}$
Squared error sum $\sum_i^{12} (v_{\text{obs}} - v_{\text{cal}}^i)^2 = 382.09 \text{ cm}^{-2}$

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**Figure 2.** Cross-sections of the potential function  $V_0(\rho_1, \rho_3)$ . The broken curve represents  $V_0$  at  $\rho_1 = \rho_1^e = 1.5525 \text{ \AA}$ ,  $\rho_3 = 0$ . The solid curve represents  $V_0$  at the absolute minima  $\rho_1 = \rho_1^e + \delta = 1.5641 \text{ \AA}$ ,  $\rho_3 = \pm 0.0745 \text{ \AA}$ .

$\rho_1^e + \delta + \rho_3^e = 1.6376 \text{ \AA}$  and  $\rho_1^e + \delta - \rho_3^e = 1.4906 \text{ \AA}$  (see figure 1). The barrier height is the height of the saddle point (S) above the absolute minima ( $M_1, M_2$ ):

$$\begin{aligned} \text{barrier height} &= V_0(\rho_1^e, 0) - V_0(\rho_1^e + \delta, \rho_3^e) \\ &= 1890.70 - 1760.16 = 130.54 \text{ cm}^{-1}. \end{aligned}$$

Figure 2 shows the cross sections of  $V_0(\rho_1, \rho_3)$  for  $\rho_1 = \rho_1^e$  (dashed curve) and  $\rho_1 = \rho_1^e + \delta$  (solid curve). These curves also show the saddle point (S) and the absolute



minima ( $M_1, M_2$ ). The zero point energy  $G(0,0)$  is  $618.47\text{ cm}^{-1}$  for  $S^{16}O_2$  and  $590.54\text{ cm}^{-1}$  for  $S^{18}O_2$ .

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