Effect of kinetic energy terms on the vibrational frequencies \((v_1, v_3)\) 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 \(v_1\) and \(v_3\) of \(\text{SO}_2\) in its \(^1B_2\) excited state, is discussed. Employing two large amplitude Hamiltonian \(H^0\)\((\rho_1, \rho_3)\) 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 \((\rho_1^*, \pm \rho_3^*)\) were considered. In obtaining the set 3 constants, only the two coefficients \(A\) and \(B\) evaluated at the saddle point \((\rho_1^*, 0)\) 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 \((v_1, v_3) = (0, 2), (1, 0), (1, 2), (2, 0), (0, 6)\) and \((3, 0)\) of \(S^{16}\text{O}_2\) and \(S^{18}\text{O}_2\). 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 \(S^{16}\text{O}_2\) and \(S^{18}\text{O}_2\). Subsequently, the vibrational frequencies of \(S^{16}\text{O}_2\) and \(S^{18}\text{O}_2\) 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 \(H^0(\rho_1, \rho_3)\) 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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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 $(v_1, v_3)$ 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 $(v_1, v_3)$ of SO$_2$. We obtained three sets of force fields (set 1, set 2 and set 3) each fitted to 12 frequencies of S$^{16}$O$_2$ and S$^{18}$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),

$$H_0^0(\rho_1, \rho_3) = \frac{-\hbar^2}{2\Delta_{13}^0} \left( I_{13}^0 \frac{\partial^2}{\partial \rho_1^2} - 2I_{13}^0 \frac{\partial^2}{\partial \rho_1 \partial \rho_3} + I_{11}^0 \frac{\partial^2}{\partial \rho_3^2} \right)$$

$$+ 2G \frac{\partial}{\partial \rho_1} + 2F \frac{\partial}{\partial \rho_3} + C + V_0(\rho_1, \rho_3).$$  

(1)

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

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

(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