Effect of kinetic energy terms on the vibrational frequencies \((v_1, v_3)\) in the \(^1B_2\) \((^1A')\) excited state of 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 SO\(_2\) in its \(^1B_2\) excited state, is discussed. Employing two large amplitude Hamiltonian \(H_0^a(p_1, p_3)\) 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 \((p_1, p_3)\). For set 2, only the three coefficients \(A, H,\) and \(B\), evaluated at the absolute minima \((\rho_1^a, \pm \rho_3^\pm)\) were considered. In obtaining the set 3 constants, only the two coefficients \(A\) and \(B\) evaluated at the saddle point \((\rho_1^1, 0)\) were retained. The nine force constants of the potential \(V_0(p_1, p_3)\) which includes a double minimum function in \(p_3\), 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 \(^{16}\)SO\(_2\) and \(^{18}\)SO\(_2\). 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 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 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 \(^{16}\)SO\(_2\) and \(^{18}\)SO\(_2\). Subsequently, the vibrational frequencies of \(^{16}\)SO\(_2\) and \(^{18}\)SO\(_2\) 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 \(H_0^a(p_1, p_3)\) contains a potential \(V_0(p_1, p_3)\) 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 $\text{SO}_2$. 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),

$$H^0_\alpha(\rho_1, \rho_3) = -\frac{\hbar^2}{2\Delta^6_13}\left[I^0_{33}\frac{\partial^2}{\partial \rho_1^2} - 2I^0_{13}\frac{\partial^2}{\partial \rho_1 \partial \rho_3} + I^0_{11}\frac{\partial^2}{\partial \rho_3^2}ight]
+ 2G\frac{\partial}{\partial \rho_1} + 2F\frac{\partial}{\partial \rho_3} + C
+ V^0_0(\rho_1, \rho_3).$$

(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