



Theoretical assignment of the Clements bands of SO₂



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ARTICLE INFO

Article history:

Available online 6 August 2015

Keywords:

SO₂ absorption spectrum
Clements bands
Spectral quantization
Conical intersection
Transition dipole moments

ABSTRACT

The photoabsorption spectrum of SO₂ is theoretically investigated in the energy range 3.56–4.05 eV (28713–32665 cm⁻¹). The lowest vibronic levels of the coupled excited electronic states (1¹A₂/1¹B₁) have been computed using Lanczos diagonalization of the Hamiltonian. The potential energy surfaces and the diabaticization scheme used here were already successfully applied to describe the non-adiabatic dynamics of the molecule (Lévêque et al., 2013). The important vibronic states, playing a role in the experimental spectrum, have been analyzed according to their nodal pattern to propose the first theoretical assignment of the low-energy part of the spectrum. The Clements bands A–D have been assigned and exhibit contributions from numerous transitions, in the low resolution spectrum. The overlap of these transitions is shown to provide an “accidental” regularity of the Clements bands with respect to their intensities, while their regular energy spacing (~220 cm⁻¹) results from a unique series (4, n₂, 1).

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1. Introduction

The electronic absorption spectrum of the sulfur dioxide molecule represented one of the first attempts of investigating the ultra-violet spectrum of a triatomic molecule in the 1930's. At low resolution, the absorption spectrum, in the energy range of 3.2–4.7 eV, exhibits intense, regular and sharp absorption bands, followed by an irregular plateau-like regime with roughly constant intensities and ending up at high energy with a pseudo-continuum of absorption. In the first analyses performed by Watson and Parker [1], Clements [2], Asundi and Samuel [3] and Metropolis [4], the authors pointed out that this band system results from one excited electronic state, and according to its intensity to a allowed transition. Numerous debates concerning the energy of the vibrationless transition and the assignment of the bands emerged at this time. Depending on the interpretation of the authors, the vibrationless transition could vary by 0.45 eV [4,3].

These difficulties have been partially resolved by the work of Douglas [5], who observed a Zeeman effect in the presence of a magnetic field in the low energy part of the spectrum, 3.1–3.65 eV. This effect results from a forbidden transition to a triplet excited state, determined later as a ³B₁ state by the rotational analysis of Merer [6]. This absorption band, known usually as the

“forbidden band”, masks the vibrationless transition of the allowed one. The theoretical work of Hillier and Saunders [7] provided the first SCF calculation of the molecule and predicted the presence of three triplet states and two singlet states in this energy range. The isotopic study of Brand and Nanes [8] clearly showed the two band systems belonging to the triplet states and the singlet states. But, because of the intensity of the spectrum, they discarded the possible role of a vibronic coupling between the 1¹B₁ and 1¹A₂ states to explain the absorption features. Their analysis provided a new assignment of the vibrationless transition at 3.50 eV (28 238 cm⁻¹). A few years later, the rotational analysis of Hamada and Merer [9] established a new energy of the latter at 3.46 eV (27 930 cm⁻¹), with the first experimental evidence of the primordial role of the 1¹A₂ state [10].

This long history provides the basis of our understanding of the molecular spectrum, and starting from the 1990's, a large amount of work studying the Potential Energy Surfaces (PES) of the involved states followed [11–13]. At this time the first wave-packet propagation was performed [14] and showed a fast transfer of population from the initial 1¹B₁ to the 1¹A₂ state, owing to the non-adiabatic coupling between them. New simulations [15] allowed only recently to obtain the spectrum with a good accuracy. Owing to its key role in many fields [16–18], the investigation of the photo-physics of SO₂ still attracts great experimental and theoretical interest. As an example, recently, the role of the triplet states has been investigated [19–22], and the role of the 1³B₂ state has been established theoretically and experimentally [22,20,23,24].

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In order to provide a comprehensive description of the photoabsorption spectrum, we investigate here the vibronic transitions in the low-energy part (3.56–4.05 eV) of the spectrum. The analysis of the nodal pattern of the eigenstates of the coupled ($1^1A_2/1^1B_1$) states provides us with the first theoretical assignment of the spectrum. This paper is organized as follows. We present in Section 2 the theoretical methodology used for computing the diabatic PES and for determining the eigenstates of the molecular Hamiltonian. Section 3 contains a discussion of the results obtained, followed by some concluding remarks in Section 4.

2. Computational details

2.1. Adiabatic potential energy surfaces

Here we summarize the main aspects of our methodology, which has been described in our previous work [15]. The photoabsorption spectrum can be described by considering three electronic states, namely the ground state 1^1A_1 and the two first singlet excited states 1^1B_1 and 1^1A_2 . These states have been computed using the MultiReference Configuration Interaction (MRCI) method followed by a Davidson correction [25,26]. For each state the initial wavefunction results from a state-averaged complete active space self-consistent field (CASSCF) calculation, including 18 active electrons in 12 orbitals. The molecular orbitals are described in the correlation-consistent polarized valence triple-zeta (cc-pVTZ) primitive basis set for the sulfur and oxygen atoms [27]. The relative position of the atoms is described using a combination of the internal coordinates, namely $R_s = (R_1 + R_2)/2$ and $Q_u = (R_1 - R_2)/2$, where $R_{1,2}$ stands for the distance between the sulfur and the oxygen atoms, in addition to the \widehat{OSO} angle ϕ , see Fig. 1. The variation of these three coordinates is used to build the three dimensional PES of each electronic states. In addition, the transition dipole moments between the electronic ground state and the two electronic excited states have been computed at the MRCI level as a function of the nuclear coordinates. In C_{2v} symmetry, the only allowed transition is obtained between the GS and the 1^1B_1 state, as expected from symmetry rules, but in C_s symmetry a weak transition dipole moment is obtained for the transition to the 1^1A_2 state. These dipoles are used to study the non-Condon effects in the spectrum.

The two excited electronic states 1^1B_1 and 1^1A_2 are coupled through a *symmetry-allowed* conical intersection [28], which mixes the two adiabatic states for an asymmetric distortion of the molecule. Such a distortion lowers the C_{2v} symmetry of the system to the C_s point group, where the two states are of A'' symmetry. In

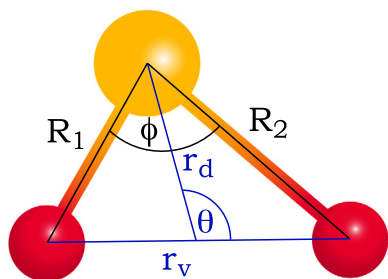


Fig. 1. Definition of the two sets of coordinates used throughout this work. In black, the two SO bond lengths R_1 and R_2 and the \widehat{OSO} angle ϕ represent the internal coordinates which have been used to compute the PES. In blue, r_v , r_d , and θ represent the Jacobi coordinates used to express the kinetic energy operator. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the C_{2v} plane ($Q_u = 0$), the two states exhibit a crossing along a *seam* for values $110 < \phi < 120^\circ$ as a function of R_s (see Fig. 2). This situation leads to a non-adiabatic coupling, resulting from the action of the nuclear kinetic energy operator on the electronic wavefunctions depending parametrically on the nuclear coordinates. This coupling exhibits a singularity at the conical intersections breaking down the Born–Oppenheimer approximation. Hence, the two electronic states must be considered together [28–31]. Moreover a numerical treatment and evaluation of the singularity is not a simple task and a transformation of the electronic basis functions to avoid such a singularity is preferable.

2.2. Diabatic Hamiltonian

The transformation from the adiabatic to a diabatic electronic basis has been performed using the regularized diabaticization scheme [32,33], which consists of an unitary transformation of the electronic basis. The advantage of this method is that the unitary transformation can be defined exclusively from the knowledge of the adiabatic PES only, and has been successfully applied for different systems [34–38]. Collecting the nuclear coordinates in a vector \mathbf{Q} , we label the regularized diabatic potential matrix of the two electronic states, $\mathbf{W}_{reg}(\mathbf{Q})$, as follows:

$$\mathbf{W}_{reg}(\mathbf{Q}) = \Sigma(\mathbf{Q})\mathbf{1} + \begin{pmatrix} d(\mathbf{Q}) & c(\mathbf{Q}) \\ c(\mathbf{Q}) & -d(\mathbf{Q}) \end{pmatrix}, \quad (1)$$

namely the sum of a diagonal matrix $\Sigma(\mathbf{Q})$ and a traceless one. The unknown elements of the diabatic potential matrix can be obtained by transforming it back to the adiabatic basis, i.e. performing a diagonalization,

$$\mathbf{V}(\mathbf{Q}) = \mathbf{S}(\mathbf{Q})^\dagger \mathbf{W}_{reg}(\mathbf{Q}) \mathbf{S}(\mathbf{Q}) \quad (2)$$

by means of a unitary transformation $\mathbf{S}(\mathbf{Q})$. The diagonal part of the diabatic potential is identified with the half sum of the adiabatic PES, $\Sigma(\mathbf{Q}) = (V_1(\mathbf{Q}) + V_2(\mathbf{Q}))/2$. The elements of the traceless matrix are linked to their half difference ($\Delta(\mathbf{Q}) = (V_1(\mathbf{Q}) - V_2(\mathbf{Q}))/2$), through the relation $\Delta(\mathbf{Q}) = \sqrt{c^2(\mathbf{Q}) + d^2(\mathbf{Q})}$. Using a first order (linear) Taylor expansion of the diabatic potential around the locus of the conical intersection (\mathbf{Q}_0) and the symmetry of the system, the elements $c(\mathbf{Q})$ and $d(\mathbf{Q})$ can be determined by,

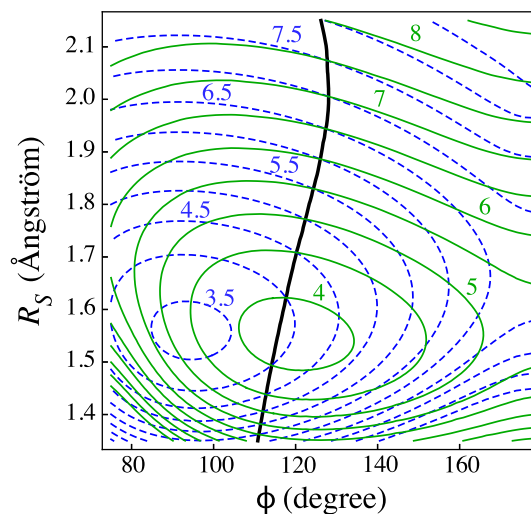


Fig. 2. Potential energy surfaces of the 1^1A_2 (dashed blue) and 1^1B_1 (green) states with respect to R_s and ϕ . The seam of conical intersections is displayed by the black line. The isolines are energetically spaced by 0.5 eV for both states. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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