

# Nonadiabatic quantum dynamics of Br<sub>2</sub> in solid Ar: A four-dimensional study of the B to C state predissociation

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## Abstract

Quantum dynamics simulations are performed for a diatomics-in-molecules based model of Br<sub>2</sub> in solid Ar which incorporates four nuclear degrees of freedom and four electronic states. The nuclear motions comprise two large amplitude coordinates describing the Br<sub>2</sub> bond distance and an effective symmetry-preserving matrix mode. Two symmetry-lowering harmonic modes are added in the spirit of linear vibronic coupling theory. Initiating the dynamics on the B state by means of an ultrafast laser pulse, nonadiabatic transitions to the two degenerate C states are monitored and the effect of vibrational preexcitation in the electronic ground state is investigated. © 2007 Elsevier B.V. All rights reserved.

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## 1. Introduction

The breakdown of the Born-Oppenheimer approximation is central to photochemical processes. A thorough understanding of the associated quantum dynamics requires knowledge about the underlying potential energy surfaces (PES) of the coupled electronic states [1]. The vibronic coupling Hamiltonian has played a decisive role, both for the general appreciation of topological features like conical intersections and for the development of dynamics methods [2,3]. The latter comprise wave packet [4–6] and density matrix propagations [7,8] as well as classical trajectory-based approaches [9]. Vibronic coupling theory is still being advanced as exemplified by recent work on an effective mode description applicable to large systems [10].

The nonadiabatic dynamics of diatomics in rare gas clusters and matrices has been studied employing mostly classical trajectory surface hopping methods [11]. Examples include the work on HCl and Cl<sub>2</sub> in Xe [12], I<sub>2</sub> in Ar [13], and F<sub>2</sub> in Ar [14]. Efforts to incorporate quantum effects on

the nuclear dynamics have been restricted to reduced, i.e., one- or two-dimensional model studies [15–17]. However, in order to describe, for instance, laser control of wave packet dynamics on coupled electronic states, a quantum approach is mandatory, see the work on spin control in Refs. [18,19]. A particularly promising route to tackle the dynamics on coupled electronic surfaces for many nuclear degrees of freedom (DOF) is the multi-configuration time-dependent Hartree (MCTDH) method [20,21]. A drawback as compared to on-the-fly trajectory-based formalisms is the necessity to determine the PES beforehand (see, however, recent developments of approximate MCTDH-type quantum methods, e.g., in Ref. [22]). For the present case of dihalogens in rare gas matrices this can only be achieved using approximations to the electronic structure as well as the choice of nuclear DOF. Here, the semiempirical diatomics-in-molecules (DIM) [23] has been shown to be particularly suited for the description of the manifold of dihalogen valence states, for an overview see Ref. [24]. As far as the nuclear DOF are concerned intuition can be successfully applied to low-dimensional cases only [15–17] and a more general strategy such as, for instance, reaction surface ideas are more promising in multi-dimensional situations [25].

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On the experimental side dihalogens in rare gas clusters and matrices at low temperatures are among the best spectroscopically characterized condensed phase molecular systems (for reviews, see Refs. [26–28]). Various types of coherence effects related to wave packet motion of the chromophore [16,29,30], of the matrix phonons [31–33] or the halogen–matrix collisions [34] have been observed. The presence of coherences lasting for hundreds of femtoseconds facilitates coherent laser control. For instance, using chirped pulse excitation the Schwentner group demonstrated the possibility of controlling wave packet revivals making it possible to extract, for instance, dephasing time scales [35]. Using phase-locked pulse pairs, it was further shown that the effective interaction between the chromophore and the matrix can be manipulated. Here, wave packets could be prepared which contained mostly contributions from either zero phonon lines or phonon side bands [36].

In this contribution we focus on the wave packet dynamics of Br<sub>2</sub> in solid Ar in the electronic B-state. Using a four-dimensional (4D) reaction surface linear vibronic coupling model developed previously in Refs. [24,25] MCTDH simulations of laser-driven dynamics have been performed with the aim to unravel mechanistic aspects of the B to C state predissociation. Here, it will be shown that matrix dynamics is important for triggering nonadiabatic transitions. This fact, although well established in principle [26], has never been investigated using multi-dimensional multi-state quantum dynamics. As a second aspect we will study the effect of vibrational preexcitation in the electronic ground state. Depending on whether a reaction coordinate or a vibronic coupling mode is initially preexcited one either observes dynamics in a different Franck–Condon region (see, e.g., Refs. [37–39]) or an increased effective nonadiabatic coupling. The paper is organized as follows: Section 2 presents the time-dependent Schrödinger equation and gives a brief account on the MCTDH setup. Numerical results are discussed in Section 3 and the paper is summarized in Section 4.

## 2. Theoretical methods

### 2.1. Reaction surface vibronic coupling hamiltonian

The DIM description of Br<sub>2</sub> in solid Ar has been detailed in Ref. [24]. Specifically, it was shown that upon restricting the range of accessible energies a reduction of the number of states for representation of the DIM Hamiltonian matrix becomes possible. In a subsequent paper, coupled potential energy surfaces targeted to describe the B state dynamics as well as the B to C state predissociation have been developed [25]. Taking into account the two-fold degeneracy of the C state as well as the electronic ground state, X, one obtains the following time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \Psi_X \\ \Psi_B \\ \Psi_C \\ \Psi_{C'} \end{pmatrix} = \begin{pmatrix} T + V_X & -\mu_{XB}\mathcal{E}(t) & 0 & 0 \\ -\mu_{BX}\mathcal{E}(t) & T + V_B & -V_{BC}^* & V_{BC'} \\ 0 & -V_{BC} & T + V_C & 0 \\ 0 & V_{BC'}^* & 0 & T + V_{C'} \end{pmatrix} \begin{pmatrix} \Psi_X \\ \Psi_B \\ \Psi_C \\ \Psi_{C'} \end{pmatrix}. \quad (1)$$

Notice that in contrast to the MO LCAO ansatz the DIM wave function consists of products of atomic functions which do not depend on the internuclear separation. In that sense they form a crude diabatic basis of zero-order states and the above matrix representation of the Hamiltonian will be termed diabatic. In Ref. [25] a minimum model PES had been developed including four nuclear degrees of freedom: (i) two large amplitude coordinates  $\zeta_R$  and  $\zeta_{X-B}$  which describe the Br<sub>2</sub> bond elongation and collective Ar cage rearrangement upon B state excitation, respectively. The effective coordinate  $\zeta_{X-B}$  incorporates rearrangements of the matrix cage when going from the ground state Br<sub>2</sub> equilibrium bond length via the B state one up to the B state outer turning point. The associated displacements resemble those observed in trajectory simulations for Cl<sub>2</sub> in Ar in Refs. [33,40]. This underlines the relevance of this coordinate not only for the long time dynamics on the B-state in the vicinity of its minimum, but also describing important aspects of the short time dynamics (see also comparison with experimentally observed phonon dynamics on a time scale of up to 6 ps in Ref. [33]).

The PES spanned by the coordinates  $\zeta_R$  and  $\zeta_{X-B}$  for the B and C states is shown in Fig. 1a. It should be noted that both coordinates preserve the approximate  $D_{2h}$  symmetry of the Br<sub>2</sub> pointing along the  $\langle 110 \rangle$  direction in its cage. Therefore, the intersection between the PES of the different states forms a crossing seam. (ii) Two harmonic linear vibronic coupling modes which are of  $B_{3g}$  ( $q_1$ ,  $\omega_1 = 60 \text{ cm}^{-1}$ ) and  $B_{2g}$  ( $q_2$ ,  $\omega_2 = 63 \text{ cm}^{-1}$ ) symmetry (see Figs. 2a and b) and which give rise to conical intersections between the B and C states as shown in Fig. 1b. In the spirit of linear vibronic coupling theory these modes can be considered to give a reasonable description in a short time domain.

The kinetic energy operator in Eq. (1) is given by

$$T = -\frac{\hbar^2}{2} \left( \frac{\partial^2}{\partial \zeta_R^2} + \frac{\partial^2}{\partial \zeta_{X-B}^2} \right) - \frac{\hbar}{2} \left( \omega_1 \frac{\partial^2}{\partial q_1^2} + \omega_2 \frac{\partial^2}{\partial q_2^2} \right) \quad (2)$$

Note, that we use mass-weighted large amplitude coordinates  $\zeta_R$  and  $\zeta_{X-B}$  and dimensionless oscillator coordinates  $q_1$  and  $q_2$ . The diagonal part of the diabatic PES in Eq. (1) reads as ( $a = X, B, C, C'$ )

$$V_a = U_a(\zeta_R, \zeta_{X-B}) + \frac{\hbar}{2} (\omega_1 q_1^2 + \omega_2 q_2^2). \quad (3)$$

In Eq. (3) the  $U_a(\zeta_R, \zeta_{X-B})$  denote the diabatic PES for the large amplitude coordinates (reaction plane) which contain

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