

# INTRAMOLECULAR DYNAMICS OF THE ROVIBRATIONAL ENERGY IN A CARBONYL SULFIDE MOLECULE

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# Abstract

We discuss the effect of low rotational excitations on intramolecular vibrational energy redistribution (IVR) in an isolated carbonyl sulfide (OCS) molecule in its electronic ground state. Computational experiments were performed to analyze the intramolecular rotational-vibrational energy redistribution (IRVR) and the intramolecular vibrational-rotational energy transfer (IVRET). We use the MCTDH software to solve the Schrödinger equation for wave packets corresponding to initial excitations on vibrational local modes. The wave packets are prepared having the same initial vibrational excitations but differing in the total angular momentum. We found that IVR is affected by  $K$ -mixing due to Coriolis coupling and that centrifugal coupling does not have a relevant role on IVR. Moreover, rotational effects on IVR depends on the vibrational bending mode. If the bending mode is not excited,  $K$ -mixing is negligible. If it is excited, then  $K$ -mixing occurs in a significant degree and as a result the wave packet evolves onto a pseudodecoherent (steady) state. However, the net redistribution does not change, i.e., on average IVR behaves in the same way. Furthermore, loss of vibrational coherence happened even when IVRET is insignificant, implying that analyzing the total vibrational energy is not fully conclusive to predict changes of IVR due to rotational excitations.

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# 1 Introduction

In chemical physics, all dynamical questions in the end lead to one: *Where does the energy go?*

Martin Gruebele

The dephasing of a rovibrational wave packet, in a sharp spin-electronic state and having a constant total angular momentum, is called *intramolecular vibrational energy redistribution* (IVR) when interest is only in the vibrational degrees of freedom (DOF's) of a molecule. Notwithstanding IVR is referred to as a phenomenon, from a wider perspective it is an area of study which can be called vibrational dynamics, i.e., the study of the temporal evolution of intramolecular vibrational DOF's in conditions of a sharp spin-electronic state and a constant total angular momentum. Because of the importance of the concept of energy in dynamics, originally, IVR has been defined in terms of it. This is accentuated by means of its pseudonym, *vibrational energy flow*. For reviews of IVR, see Refs. [1–8].

IVR has its origins in theories of unimolecular reaction rates.<sup>[7,9]</sup> Since then, study of IVR has been implied in a wide variety of topics such as classical-quantum correspondence<sup>[10–19]</sup>, control of chemical reactions<sup>[4,20–25]</sup>, electrical properties of molecular wires<sup>[26]</sup>, theories of heat conduction at a molecular level<sup>[27–30]</sup>, quantum computing<sup>[31–37]</sup>, functionality of residues in proteins<sup>[38]</sup> and positron annihilation mechanisms<sup>[39]</sup>. The study of IVR itself has led to progress in both theoretical and experimental fields. Different experimental methodologies<sup>[6,40–51]</sup> has been designed or applied to “see” IVR, for a recent review see Ref. [1]. On the theoretical side, there are two quite extended models to rationalize IVR. Namely, the tier model<sup>[52–58]</sup> and the state space model<sup>[59–65]</sup>, the latter being a general model which includes the tier model perspective. Moreover, as monitoring “vibrational energy flow” is not a

straight procedure as it may seem, proposals for gaining insight on IVR has also been developed [66–68].

“Understanding” IVR, as any radiationless molecular process, starts by the definition of a zero-order Hamiltonian. [69] Then, starting from the standard Born-Oppenheimer approximation, the next step is to define a zero-order vibrational Hamiltonian. This zero-order vibrational Hamiltonian is separable into  $3N - 6$  vibrational modes, where  $N$  is the number of nuclei. Hence, the temporal evolution of the initial non-stationary excited vibrational state is interpreted in relation to these vibrational modes. Because of the great importance of the rectilinear normal modes of vibration in the interpretation of the rovibrational structure of molecules, this is by far the preferred zero-order model. Nevertheless, any zero-order model can be used. Hence, IVR is zero-order model dependent [70,71] and clearly initial state dependent as well.

Even though the first experimental demonstration of IVR supported the RRKM theory, latter experimental demonstrations of IVR emerged refuting the statistical redistribution assumed in the RRKM theory. Nowadays, it is common to find extremely slow IVR rates. [72–75] Then, an important aspect in IVR emerges, i.e., different regimes [5,7,25] of IVR, namely, no IVR, restricted IVR, and dissipative IVR, which are not necessarily related with low, medium and high energy regimes. [76–79] Currently, by means of the state space model special interest has emerged in the transition from a restricted IVR to an ergodic or facile IVR. [13,59] Implicitly, these regimes are defined for IVR of an initial state chosen as a zero-order state where the zero-order model approximates the molecular eigenstates at low energy. This is why rectilinear normal modes of vibration are commonly used in IVR. Hence, when no IVR is found at low energies, it is because the initial excited state corresponds approximately to a molecular eigenstate (stationary respect to IVR). However, this does not exclude the possibility of creating an initial wave packet of low energy for which IVR occurs.

Mostly, IVR has been studied for a total angular momentum equal to zero. Yet, many experimental investigations about the effect of rotations on IVR have been reported, for

example Refs. [80–92]. These investigations have led to the conclusion that depending on the system, rotational excitations can affect IVR. Theoretical investigations have exposed different mechanisms involved in the disturbance of IVR by rotational excitations. Namely, *K-mixing* <sup>[93,94]</sup> due to Coriolis coupling and *vibrationally induced rotational axis switching* (VIRAS) mechanism <sup>[95]</sup>, and *K*-preserving mechanisms as a centrifugal coupling mechanism <sup>[96,97]</sup> and the *rotationally induced vibrational mixing* (RIVR) <sup>[98–100]</sup> due to a type of Coriolis coupling.

## 2 Methodology

### 2.1 Theoretical aspects

#### 2.1.1 Quantum numbers and non-stationary states: How do we think of IVR?

We use a framework based on non-relativistic quantum mechanics and the Born-Oppenheimer approximation. Then, a molecule (our system) can be defined as a collection of particles,  $N$  nuclei, with no internal structure and no charge, subject to the action of a field, the potential energy surface (PES). Regarding a particular electronic state and a particular total spin state, the nuclear state  $|\Psi(t)\rangle$  is governed by the Schrödinger equation (atomic units are assumed throughout the text):

$$i|\dot{\Psi}(t)\rangle = \hat{H}|\Psi(t)\rangle, \quad (2.1)$$

where  $\hat{H}$  is the translationally invariant nuclear Hamiltonian given by the sum of the kinetic energy operator (KEO) for nuclei,  $\hat{T}$ , and the PES operator,  $\hat{V}$ .

A *completely* isolated system is assumed, i.e., we suppose the system is isolated from matter and electromagnetic field. Hence,  $\hat{H} \neq \hat{H}(t)$  and  $|\psi_n(t)\rangle$  are all stationary states, not just the ground state, where

$$\hat{H}|\psi_n(t)\rangle = E_n|\psi_n(t)\rangle, \quad n \in [0, \infty) \quad (2.2)$$

and  $|\psi_n(t)\rangle = |\psi_n\rangle e^{-iE_n t}$ . Isolation implies isotropy of the space for the molecule; therefore,  $n$  can be exactly separated into three quantum numbers, namely,  $J$ ,  $M$  and  $n'$ , where  $J$  and  $M$  are associated with the rotational DOF's and  $n'$  involves vibrational and rotational DOF's.

$J$  is related to the total nuclear angular momentum magnitude by means of

$$\hat{J}^2|\psi_{J,M,n'}\rangle = J(J+1)|\psi_{J,M,n'}\rangle, \quad (2.3)$$

where  $\hat{J}$  is the total nuclear angular momentum operator.  $M$  is related to the magnitude of the component of the total nuclear angular momentum in the space-fixed (SF) frame  $z$ -axis, by means of

$$\hat{J}_z^{SF} |\psi_{J,M,n'}\rangle = M |\psi_{J,M,n'}\rangle, \quad (2.4)$$

where  $\hat{J}_z^{SF}$  is the operator form of the component of the total nuclear angular momentum in the SF-frame  $z$ -axis.

Analyzing IVR requires the definition of separated vibrations, i.e.,  $n'$  has to be split into a collection of  $3N - 6$  vibrational quantum numbers  $(n_1, \dots, n_{3N-6})$  and a rotational quantum number  $(n_r)$ . Strictly speaking, this separation is not exact, i.e.,

$$|\psi_{J,M,n'}\rangle \neq |\varphi_{J,M,n_1,\dots,n_{3N-6},n_r}\rangle \quad (2.5)$$

but

$$|\psi_{J,M,n'}\rangle = \sum_{n_1,\dots,n_{3N-6},n_r} c_{n_1,\dots,n_{3N-6},n_r} |\varphi_{J,M,n_1,\dots,n_{3N-6},n_r}\rangle, \quad c_{n_1,\dots,n_{3N-6},n_r} \in \mathbb{C}. \quad (2.6)$$

Usually, but not necessarily

$$|\varphi_{J,M,n_1,\dots,n_{3N-6},n_r}\rangle = |J, M\rangle \otimes |n_1\rangle \dots \otimes |n_{3N-6}\rangle \otimes |n_r\rangle, \quad (2.7)$$

where

$$\hat{H}_i |n_i\rangle = \epsilon_{n_i} |n_i\rangle, \quad n_i \in [0, \infty), \quad i \in \{1, \dots, 3N - 6, r\}, \quad \epsilon_{n_i} < \epsilon_{n_i+1}. \quad (2.8)$$

The one dimensional Hamiltonians  $\hat{H}_i$  are related to the  $3N - 3$  dimensional Hamiltonian  $\hat{H}$  by

$$\hat{H} = \hat{H}^0 + \hat{H}_C, \quad (2.9)$$

where

$$\hat{H}^0 = \hat{H}_R + \hat{H}_r + \sum_{i=1}^{3N-6} \hat{H}_i \quad (2.10)$$

and  $\hat{H}_C$  includes the terms involving coupling between the different DOF's.  $\hat{H}_R$  includes the rotational DOF's other than the associated with  $n_r$ . Depending on the wanted type of analysis,  $\hat{H}_R$  and  $\hat{H}_r$  could be joined with  $\hat{H}_C$ . The scenario dictated by  $\hat{H}^0$  where  $|\varphi_{J,M,n_1,\dots,n_{3N-6},n_r}\rangle$  are stationary states is called a zero-order model.<sup>I</sup>

Now, assume  $J = M = n_r = 0$ . Then, a vibrational wave packet  $|\Upsilon(t)\rangle$  can be written as

$$\begin{aligned} |\Upsilon(t)\rangle &= \sum_{n'} a_{n'} |\psi_{0,0,n'}(t)\rangle \\ &= \sum_{n'} a_{n'} \left( \sum_{n_1,\dots,n_{3N-6}} c_{n_1,\dots,n_{3N-6},0}^{(n')} |\varphi_{0,0,n_1,\dots,n_{3N-6},0}\rangle \right) e^{-iE_{J=0,n'}t} \\ &= \sum_{n_1,\dots,n_{3N-6}} \left( \sum_{n'} a_{n'} c_{n_1,\dots,n_{3N-6},0}^{(n')} e^{-iE_{J=0,n'}t} \right) |\varphi_{0,0,n_1,\dots,n_{3N-6},0}\rangle \\ &\equiv \sum_{n_1,\dots,n_{3N-6}} b_{n_1,\dots,n_{3N-6},0}(t) |\varphi_{0,0,n_1,\dots,n_{3N-6},0}\rangle, \end{aligned} \quad (2.11)$$

where  $a_{n'} \in \mathbb{C}$ . Eq. 2.11 shows the importance of a zero-order description in IVR, i.e., a zero-order model allows the interpretation of IVR in terms of transitions between states of specific vibrational modes. In this way, the transfer of population through the different  $|\varphi_{0,0,n_1,\dots,n_{3N-6},0}\rangle$  can be monitored, i.e., the vibrational energy flow. Consequently, an important part of IVR research has dealt with clarifying the mechanism by which IVR proceeds, i.e., the determination of which  $|\varphi_{J,M,n_1,\dots,n_{3N-6},n_r}\rangle$  are coupled (IVR pathways), the dilucidation of the terms in  $\hat{H}_C$  which are responsible for coupling different  $|\varphi_{J,M,n_1,\dots,n_{3N-6},n_r}\rangle$  and the description of the time scales in which this coupling proceeds. The  $b_{n_1,\dots,n_{3N-6},0}(t)$  for a general rovibrational wave packet is given by  $\sum_{J,M,n'} a_{J,M,n'} c_{n_1,\dots,n_{3N-6},n_r}^{(J,M,n')} e^{-iE_{J,M,n'}t}$ . Hence, rotational DOF's bring new vibrational manifolds, and therefore, new IVR pathways. That is why rotations become interesting in IVR analysis.

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<sup>I</sup>On account of perturbation theory in which  $\hat{H}^0$  would be the zeroth-order term to describe  $\hat{H}$ .

The standard approach<sup>I</sup> in IVR research has been to assume that the excited state is fully described by a zero-order state, i.e.,  $|\Upsilon(0)\rangle = |\varphi_{J,M,n_1,\dots,n_{3N-6},n_r}\rangle$ . However,  $\{n_1, \dots, n_{3N-6}, n_r\}$  are not good quantum numbers, i.e., separable vibrations are fictitious. Then, after excitation,  $|\varphi_{J,M,n_1,\dots,n_{3N-6},n_r}\rangle$  mixes with other zero-order states; this mixing is described by each  $b_{n_1,\dots,n_{3N-6},n_r}(t)$ .

### 2.1.2 System and zero-order description: What molecule are we interested in?

The system we analyze is a triatomic linear molecule. Specifically, it is a completely isolated carbonyl sulfide (OCS) molecule in the electronic ground state. In contrast with other work done on IVR for OCS, [78, 79, 101–104] we employed the more recent and accurate PES reported in Ref. [105].

Our vibrational zero-order model is based on a separation in local modes [106], this local modes are associated with bond lengths and angles between bonds. Then, our vibrational DOF's correspond to a vibration of the bond between the carbon and the sulfur nuclei, a vibration of the bond between the carbon and the oxygen nuclei and a vibration of the bending motion between both bonds. We will refer to these vibrational modes as the *CS*, *OC* and  $\theta$  modes, respectively.

Linear molecules are particularly interesting for the study of IVR subject to rotational excitations, as there is a strong coupling between the  $\theta$  mode and the rotation around the internuclear axis at the collinear configuration, i.e., the axis of the smallest moment of inertia. This strong coupling, as compared with a bent triatomic molecule, is due to a singularity emerging from the KEO at the collinear configuration, which, for a linear molecule, is the minimum of the PES. On account of this strong coupling, it is practical

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<sup>I</sup>An approach inherited from one of the IVR “parents”: Molecular spectroscopy.

to use a separation of the form:

$$|\varphi_{J,M,n_{CS},n_{OC},n_{\theta},n_r}\rangle = |J, M\rangle \otimes |n_{CS}\rangle \otimes |n_{OC}\rangle \otimes |n_{\theta}n_r\rangle, \quad (2.12)$$

where

$$\hat{H}_{\theta r} |n_{\theta}n_r\rangle = \epsilon_{n_{\theta r}} |n_{\theta}n_r\rangle, \quad n_{\theta r} \in [0, \infty), \quad \epsilon_{n_{\theta r}} < \epsilon_{n_{\theta r}+1}. \quad (2.13)$$

Moreover, we decide to use  $n_r \equiv n_K = K$ , where  $K$  is the quantum number related to the magnitude of the component of the total nuclear angular momentum in the body-fixed (BF) frame  $z$ -axis. Hence, the angular momentum eigenstates  $|J, M, K\rangle$  can be used as a basis set for the rotational DOF's. These are the eigenstates of  $\hat{J}$ ,  $\hat{J}_z^{SF}$  and  $\hat{J}_z^{BF}$ , where  $\hat{J}_z^{BF}$  is the operator form of the component of the total nuclear angular momentum in the BF-frame  $z$ -axis. Moreover, we define  $\hat{H}_{\theta K}$  such that  $\hat{H}_{\theta K} = \hat{H}_{\theta K}(j_z^{BF})$  and  $[\hat{H}_{\theta K}, \hat{J}_z^{BF}] = 0$ . Therefore,

$$|\varphi_{J,M,n_{CS},n_{OC},n_{\theta},K}\rangle = |J, M, K\rangle \otimes |n_{CS}\rangle \otimes |n_{OC}\rangle \otimes |n_{\theta}(K)\rangle, \quad (2.14)$$

where  $|n_{\theta}(K)\rangle$  is a one dimensional state depending parametrically on  $K$ .

It is worth to mention that the electronic ground state has no electronic angular momentum. Hence, the nuclear angular momentum operators, mentioned so far, can be taken to be the *total* angular momentum operators.

### 2.1.3 Initial conditions: How do we “turn on” the IVR?

The process that produces the wave packet will not be discussed, only the wave packet evolution after its creation. A vibrational wave packet having a sharp  $J$  will be proposed, i.e.,

$$|\Phi_J(t)\rangle = \sum_{M,n'} a_{M,n'} |\psi_{J,M,n'}(t)\rangle, \quad a_{M,n'} \in \mathbb{C}. \quad (2.15)$$

Taking into account that  $\hat{H}$  depends on  $\hat{J}$  but not on  $\hat{J}_z^{SF}$ , the  $M$  components in  $|\Phi_J(t)\rangle$  can be ignored as they do not affect the dynamics if the wave packet is sharp in  $M$ , i.e.,  $a_{M,n'} = 0$  for all but one  $M$  or if the other DOF's but the one corresponding to  $M$  are in the same state for each  $M$  component, i.e.,  $|\Phi_J(t)\rangle = \sum_M a_{M,n'} |\psi_{J,M,n'}(t)\rangle$ . Then, for our purposes

$$|\Phi_J(t)\rangle = \sum_{n'} a_{n'} |\psi_{J,n'}(t)\rangle, \quad a_{n'} \in \mathbb{C} \quad (2.16)$$

and  $\langle M \rangle = \langle \Phi_J(t) | \hat{J}_z^{SF} | \Phi_J(t) \rangle$  is a time-independent value, which is not necessary to be known. Two initial conditions will be compared, namely, a vibrational wave packet having  $J = 0$  and  $J = 10$ .

Regarding the rotational DOF involved in  $n'$ , a wave packet with just one initial  $K = 0$  component will be chosen, i.e.,

$$|\Phi_{10}(0)\rangle = \sum_{n_{CS}, n_{OC}, n_\theta} c_{n_{CS}, n_{OC}, n_\theta, 0} |\varphi_{J, n_{CS}, n_{OC}, n_\theta, 0}\rangle. \quad (2.17)$$

Taking into account that  $\hat{H} = \hat{H}(\hat{J}_+^{BF} + \hat{J}_-^{BF}, \hat{J}_+^{BF} - \hat{J}_-^{BF})$ , where

$$\hat{J}_\pm^{BF} \equiv \hat{J}_x^{BF} \pm i\hat{J}_y^{BF} \quad (2.18)$$

are the ladder operators, the initial condition  $K = 0$  implies that  $\langle K \rangle = \langle \Phi_J(t) | \hat{J}_z^{BF} | \Phi_J(t) \rangle$  is equal to zero at all times. The motivation for choosing the initial condition  $K = 0$  comes from the linear rigid rotor model, where  $K$  is a good quantum number and strictly it has a single value equal to zero.

Now, with regard to the vibrational DOF's involved in  $n'$ , a predominant excitation in one vibrational mode at  $t = 0$  will be defined. In order to do it, the standard approach in IVR for defining the vibrational wave packet will be used, i.e., at  $t = 0$  it will be an eigenstate of the zero-order vibrational Hamiltonian,  $\hat{H}_V^0 \equiv \sum_{i=1}^{3N-6} \hat{H}_i$  (see Eqs. 2.9 and

2.10). Specifically, we choose it to be an edge state, i.e.,

$$|\Phi_J(0)\rangle = |\varphi_{J,n_{CS},n_{OC},n_\theta,0}\rangle = |J,0\rangle \otimes |n_{CS}\rangle \otimes |n_{OC}\rangle \otimes |n_\theta(0)\rangle, \quad (2.19)$$

where  $n_i = 0$  for all but one vibrational mode,  $i \in \{CS, OC, \theta\}$ .

On account of the initial condition, our research can be classified as an investigation on what previously was termed<sup>I</sup> *intramolecular rotational-vibrational energy redistribution* (IRVR)<sup>II</sup>, which is defined as the redistribution “*of localized, mode or bond specific vibrational excitation energy among the different internal degrees of freedom of a molecule*”.<sup>[107]</sup>

#### 2.1.4 Analysis tools: How do we “watch” the IVR?

The IVR undergone by the wave packet evolution is monitored by means of the local mode energies. They are defined by means of

$$\langle E_i \rangle = \langle \Phi_J(t) | \hat{H}_i | \Phi_J(t) \rangle, \quad i \in \{CS, OC, \theta\}. \quad (2.20)$$

$\hat{H}_\theta \equiv \hat{H}_{\theta K}$ , where  $K = 0$ . We also include the vibrational coupling, i.e.,

$$\langle E_C \rangle = \langle \Phi_J(t) | \hat{H}_C^{(V)} | \Phi_J(t) \rangle \equiv \langle \Phi_J(t) | \left( \hat{H}_V - \hat{H}_V^0 \right) | \Phi_J(t) \rangle. \quad (2.21)$$

The vibrational Hamiltonian  $\hat{H}_V$  is defined as

$$\hat{H}_V \equiv \langle J, K, M | \hat{H} | J, K, M \rangle, \quad (2.22)$$

where  $J = M = K = 0$ .

Notice that for a wave packet  $|\Phi_0(t)\rangle$ ,  $\langle E_V \rangle$  is independent of time. But for  $|\Phi_{J \neq 0}(t)\rangle$ ,  $\langle E_V \rangle$  depends on time. This is because for  $|\Phi_0(t)\rangle$ ,  $\langle E_V \rangle = \langle H \rangle$ . In the case of  $|\Phi_{J \neq 0}(t)\rangle$ ,

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<sup>I</sup>Originally, it was called intramolecular rotation-vibration redistribution. We include “energy”.

<sup>II</sup>Do not confuse with RIVR.

$\langle E_V \rangle \neq \langle H \rangle$ . Then, apart from monitoring IVR is also useful to monitor the total vibrational energy and the total rotational energy, i.e., to analyze the so-called *intramolecular vibrational-rotational energy transfer* (IVRET). IVRET is defined<sup>I</sup> as “*the flow of energy between rotation and vibration within an isolated molecule, caused by centrifugal and Coriolis forces*”.<sup>[108]</sup> Thus, we split the total energy in four terms: a purely vibrational energy,  $\langle E_V \rangle$ , a rotational energy,<sup>II</sup>  $\langle E_R \rangle$ , a Coriolis coupling energy,  $\langle E_{VR} \rangle$ , and a term we called asymmetric rotational energy,<sup>III</sup>  $\langle E_{AR} \rangle$ . Then,

$$\langle H \rangle = \langle E_V \rangle + \langle E_R \rangle + \langle E_{VR} \rangle + \langle E_{AR} \rangle, \quad (2.23)$$

where Eq. 2.20 holds for  $i \in \{V, R, VR, AR\}$ .

In addition, we use population in  $K$ -states,  $P_K(t)$ , as an indication and quantification of  $K$ -mixing<sup>IV</sup>. This is defined as

$$P_K(t) \equiv \langle \Phi_J(t) | \hat{P}_K | \Phi_J(t) \rangle, \quad (2.24)$$

where  $\hat{P}_K = \hat{1} \otimes |K\rangle \langle K| \otimes \hat{1}$  and  $\hat{1}$  represents an identity operator over the rest of DOF's.

## 2.2 Computational aspects

We solve the Schrödinger equation numerically. Then, a coordinate representation is indispensable. In coordinate representation, the chosen vibrational local modes have a one-to-one relation with valence curvilinear coordinates.  $\hat{H}_i$ , for  $i \in \{CS, OC, \theta K, V, R, VR, AR\}$ , is shown in coordinate representation in Appendix I. The definition of rotational coordinates requires the definition of a BF-frame. This frame can be defined in various ways, then the meaning of  $K$  is BF-frame dependent. To interpret  $K$ , we show the BF-frame in Appendix I.

<sup>I</sup>Originally, it was defined as “*the flow of large amounts of energy...*”. We omit “*of large amounts*”.

<sup>II</sup>In the form we define the rotational energy, it depends also on the vibrational DOF's.

<sup>III</sup>This rotational energy also is defined in such a way that it depends on vibrational DOF's.

<sup>IV</sup> $K$ -mixing will be discussed in next section.

The Schrödinger equation is solved using the MCTDH package,<sup>[109]</sup> which is an implementation of the multiconfiguration time-dependent Hartree (MCTDH) method.<sup>[110,111]</sup> Briefly speaking, the MCTDH approach uses a spectral representation of the wave function,  $\Psi(\vec{r}, t)$ , in terms of the so-called single particle functions,  $\phi_{n_k, k}(\vec{r}, t)$ , i.e.,

$$\Psi(\vec{r}, t) = \sum_{n_1=1} \dots \sum_{n_k=1} a_{n_1 \dots n_k}(t) \prod_{k=1}^{3N-6} \phi_{n_k, k}(\vec{r}, t). \quad (2.25)$$

A variational principle is implemented to derive the equations of motion for  $a_{n_1 \dots n_k}(t)$  and  $\phi_{n_k, k}(\vec{r}, t)$ . The single particle functions are represented in a pseudospectral basis set, the so-called (time-independent) primitive functions. Particularly, we choose a DVR basis set for each DOF as the primitive functions.

### 3 Discussion

#### 3.1 Warming up: Rotationally mediated IVR mechanisms

Before running the computational experiments, we will determine for our system which couplings are involved in the IVR mechanisms mediated by rotations, namely,  $K$ -mixing and the  $K$ -preserving mechanisms. In order to do it, let us analyze  $\hat{H}$  to infer which terms could couple our initial state  $|\Phi_J(0)\rangle = |\varphi_{J,n_{CS},n_{OC},n_\theta,K}\rangle$  to the rest of the zero-order states. For analyzing these mechanisms,  $\hat{H}$  can conveniently be written in terms of the angular momentum operators. Hence:

$$\begin{aligned} \hat{H} = & \hat{H}_V + \hat{A}\hat{J}^2 + \hat{B}\left(\hat{J}_z^{BF}\right)^2 + \hat{C}\left(\hat{J}_+^{BF} - \hat{J}_-^{BF}\right) \\ & + \hat{D}\left(\left[\hat{J}_+^{BF}, \hat{J}_z^{BF}\right]_+ + \left[\hat{J}_-^{BF}, \hat{J}_z^{BF}\right]_+\right), \end{aligned} \quad (3.1)$$

where  $\hat{A}$ ,  $\hat{B}$ ,  $\hat{C}$  and  $\hat{D}$  are operators depending on the vibrational DOF's only (see Appendix I) and  $[\ , \ ]_+$  stands for anticommutator.  $\hat{A}$ ,  $\hat{B}$ , and  $\hat{D}$  depend on position operators and  $\hat{C}$  depends on momentum operators. Taking into account that

$$\begin{aligned} \hat{J}^2 |J, M, K\rangle &= J(J+1) |J, M, K\rangle, \\ \hat{J}_z^{BF} |J, M, K\rangle &= K |J, M, K\rangle, \\ \hat{J}_\pm^{BF} |J, M, K\rangle &= C_{J,K}^\mp |J, M, K \mp 1\rangle, \end{aligned} \quad (3.2)$$

where  $C_{J,K}^\pm = \sqrt{J(J+1) - K(K \pm 1)}$ , we see that  $\hat{A}\hat{J}^2$  will provide a constant effective (centrifugal) term to the dynamics and  $\hat{B}\left(\hat{J}_z^{BF}\right)^2$  will provide a  $K$ -dependent effective (centrifugal) term. The expectation value of these two terms is what we called rotational energy as they resemble the Hamiltonian of a symmetric rigid rotor. Both terms can couple different zero-order vibrational states but not different zero-order rotational states, so they are responsible for what we call a  $K$ -preserving mechanism.

The last two terms provide the mixing between different rotational states as they have

the ladder operators,  $\hat{J}_+^{BF}$  and  $\hat{J}_-^{BF}$ . Therefore, they are responsible for the so-called  $K$ -mixing mechanism. The expectation value of  $\hat{C} \left( \hat{J}_+^{BF} - \hat{J}_-^{BF} \right)$  is what we called the Coriolis coupling energy. This term is the Coriolis coupling as it couples vibrational and rotational momenta. The expectation value of  $\hat{D} \left( \left[ \hat{J}_+^{BF}, \hat{J}_z^{BF} \right]_+ + \left[ \hat{J}_-^{BF}, \hat{J}_z^{BF} \right]_+ \right)$  is what we called the asymmetric rotational energy, as together with the rotational energy resembles the Hamiltonian of an asymmetric rigid rotor where  $K$  is not a good quantum number. The VIRAS mechanism for mixing  $K$ -states can be attributed to this term, which we will refer to as the asymmetric rotor coupling.

### 3.1.1 $K$ -mixing

$K$ -mixing is the deterioration of the approximate goodness of the quantum number  $K$ , i.e., the deviation from the rigid rotor model. Although  $K$ -mixing is focussed on the rotational DOF's, it is of paramount importance for IRVR as each different  $K$  brings a whole manifold of vibrational states which, in principle, could substantially change IVR as compared with IVR at  $J = 0$ .

Taking into account only the rotational DOF's, our initial state is  $|\Phi_J(0)\rangle = |JK\rangle$ . Given that

$$|\Phi_J(t)\rangle = e^{-i\hat{H}t} |\Phi_J(0)\rangle = \sum_{p=0}^{\infty} \frac{1}{p!} \left( -it\hat{H} \right)^p |\Phi_J(0)\rangle, \quad (3.3)$$

at an infinitesimal time after  $t = 0$ , the wave packet will have evolved to

$$|\Phi_J(dt)\rangle \approx |\Phi_J(0)\rangle - idt \left| \hat{H}\Phi_J(0) \right\rangle. \quad (3.4)$$

Thus, the first components having  $K \neq 0$  can be known by operating  $\hat{H}$  into  $|\Phi_J(0)\rangle$ . Then, on account of the Coriolis coupling

$$\left( \hat{J}_+^{BF} - \hat{J}_-^{BF} \right) |J, K\rangle = C_{J,K}^- |J, K-1\rangle + C_{J,K}^+ |J, K+1\rangle \quad (3.5)$$

and on account of the asymmetric rotor coupling

$$\left( \left[ \hat{J}_+^{BF}, \hat{J}_z^{BF} \right]_+ + \left[ \hat{J}_-^{BF}, \hat{J}_z^{BF} \right]_+ \right) |JK\rangle = (2K-1) C_{J,K}^- |J, K-1\rangle + (2K+1) C_{J,K}^+ |J, K+1\rangle. \quad (3.6)$$

Now, it is worth to notice that depending on the initial  $K$  component of the wave packet, the mechanism of  $K$ -mixing can be ascribed mostly to the asymmetric rotor coupling, i.e., to the VIRAS mechanism. This can be seen by analyzing the dependence on  $K$  of  $C_{J,K}^-$  and  $C_{J,K}^+$  contrasted with  $(2K-1) C_{J,K}^-$  and  $(2K+1) C_{J,K}^+$ . Fig. 1 shows that for an initial condition  $|\Phi_{10}(0)\rangle = |\varphi_{10,n_{CS},n_{OC},n_{\theta},K}\rangle$  and for  $5 \lesssim K \lesssim 10$  the term which (initially and) mostly breaks the goodness of the quantum number  $K$  is mainly the asymmetric rotor coupling. Notice that we are assuming that  $\hat{C}|\Phi_{10}(0)\rangle$  and  $\hat{D}|\Phi_{10}(0)\rangle$  are independent of the initial  $K$ , which is indeed a good approximation even when the  $K$ -dependence of the  $\theta$  mode is taken into account.<sup>I</sup>

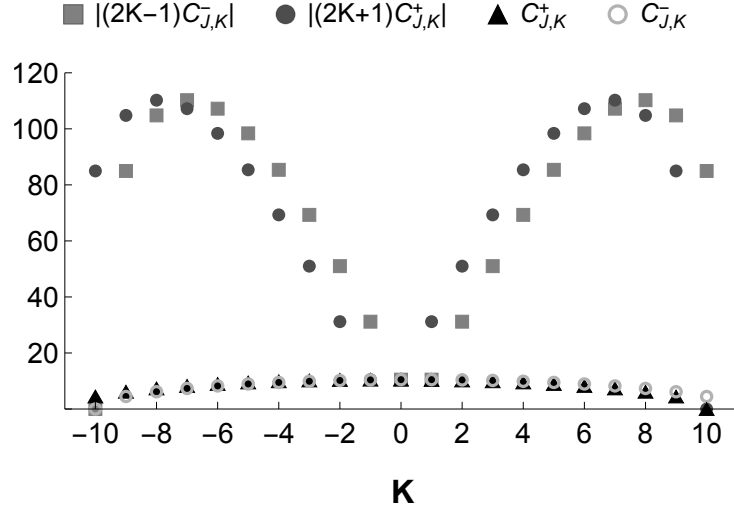


Figure 1:  $C_{J,K}^+$ ,  $C_{J,K}^-$ ,  $|(2K-1) C_{J,K}^-|$  and  $|(2K+1) C_{J,K}^+|$  as functions of  $K$  for  $J = 10$ .

Fig. 1 also shows that Coriolis coupling is approximately independent of  $K$ . Moreover, for our type of initial state, i.e., an initial  $K = 0$  component, it can be seen that both kinds of coupling will contribute equally to the initial  $K$ -mixing mechanism.

<sup>I</sup>Some tests were carried out using the harmonic approximation.

### 3.1.2 $K$ -preserving mechanisms

RIVR is a mechanism based on coupling of vibrational angular momentum and  $\hat{J}_z^{BF}$ . Then, in triatomic molecules it is absent as the vibrational angular momentum is not present (this corresponds to  $\hat{J}_z^{BF}$ ). If we followed the standard approach of gathering the rotation around the BF-frame  $z$ -axis together with the vibrations to define four “vibrations”, the “vibrational” angular momentum emerges but  $\hat{J}_z^{BF}$  disappears. Then, a term coupling the “vibrational” angular momentum and  $\hat{J}_z^{BF}$  would be absent as well.

Regarding centrifugal coupling, IVR can be affected by rotational excitations due to differences in the vibrational manifold corresponding to  $(J, K) \neq (0, 0)$  as compared with the  $(J, K) = (0, 0)$  manifold. The IVR pathways at  $J = 0$  represented by the population flow  $|\varphi_{0,n_{CS},n_{OC},n_{\theta},0}\rangle \rightarrow \{|\varphi_{0,n_{CS},n_{OC},n_{\theta},0}\rangle\}$  can, in principle, be different from  $|\varphi_{J \neq 0,n_{CS},n_{OC},n_{\theta},K}\rangle \rightarrow \{|\varphi_{J \neq 0,n_{CS},n_{OC},n_{\theta},K}\rangle\}$ , where  $\{|\varphi_{J,n_{CS},n_{OC},n_{\theta},K}\rangle\}$  runs over all combinations of  $n_{CS}, n_{OC}, n_{\theta}$ .

## 3.2 Computational experiments: Vibrational energy flow in OCS

### 3.2.1 Bond excitations

Fig. 2 shows the evolution of  $|\Phi_0(0)\rangle = |\varphi_{0,10,0,0,0}\rangle$  and  $|\Phi_0(0)\rangle = |\varphi_{0,0,6,0,0}\rangle$  vs. the evolution of  $|\Phi_{10}(0)\rangle = |\varphi_{10,10,0,0,0}\rangle$  and  $|\Phi_{10}(0)\rangle = |\varphi_{10,0,6,0,0}\rangle$ . These wave packets have an energy of about 30% of the dissociation threshold, which corresponds to the CS bond dissociation energy. The results show that IVR is not affected by a rotational excitation with  $J = 10$  and  $\langle K \rangle = 0$ .<sup>I</sup> A straightforward explanation could be that the rotational excitation is too low. This is confirmed by analyzing the IVRET. Fig. 3 displays the different contributions to the total energy as defined in the methodology (see Eq. 2.23).

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<sup>I</sup>As mentioned in the methodology this is the only rotational excitation we will consider. Then, if not necessary, hereafter we will not indicate the type of the rotational excitation, which is implicit.

From Fig. 3 it is noted that the vibrational energy is not significantly perturbed, what can be ascribed to a low rotational energy.

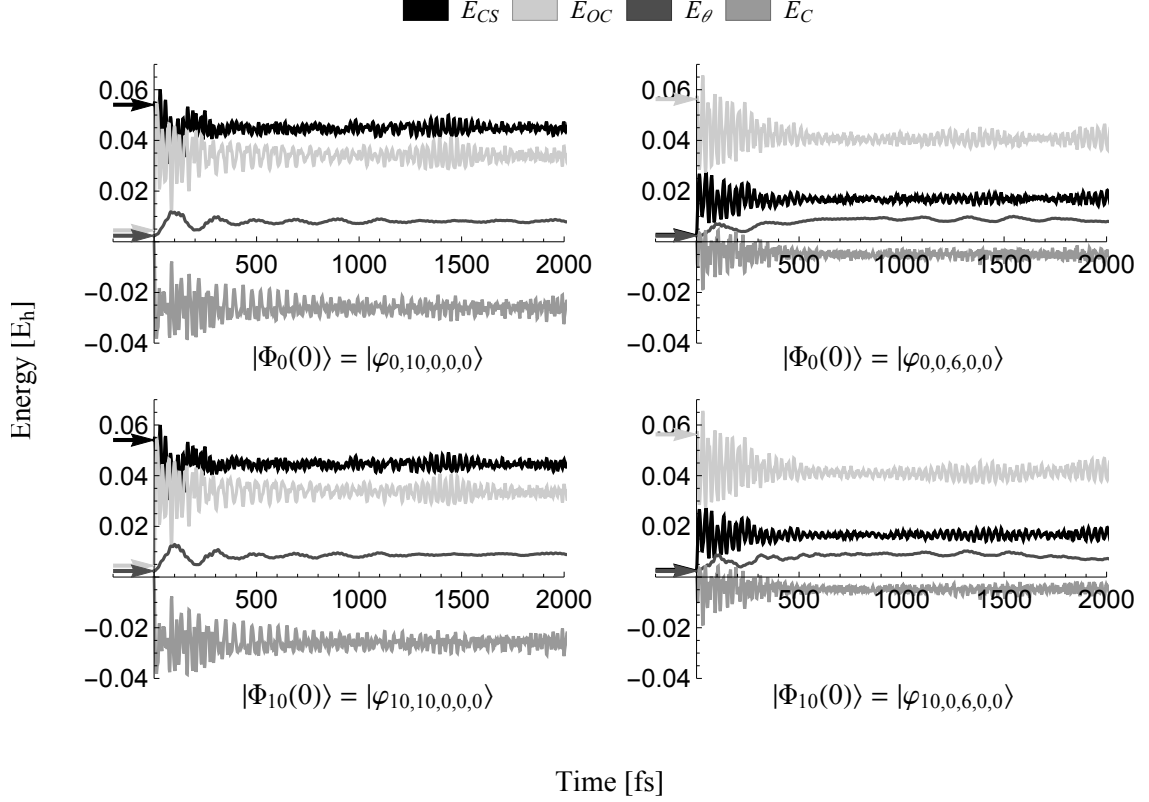


Figure 2:  $\langle E_i \rangle$  for  $i \in \{CS, OC, \theta, C\}$ , for the temporal evolution of  $|\Phi_J(0)\rangle \in \{|\varphi_{J,10,0,0,0}\rangle, |\varphi_{J,0,6,0,0}\rangle\}$  with  $J \in \{0, 10\}$ . Arrows show the initial value of  $\langle E_i \rangle$ , except for  $\langle E_C \rangle$  which is always equal to 0 at  $t = 0$ .

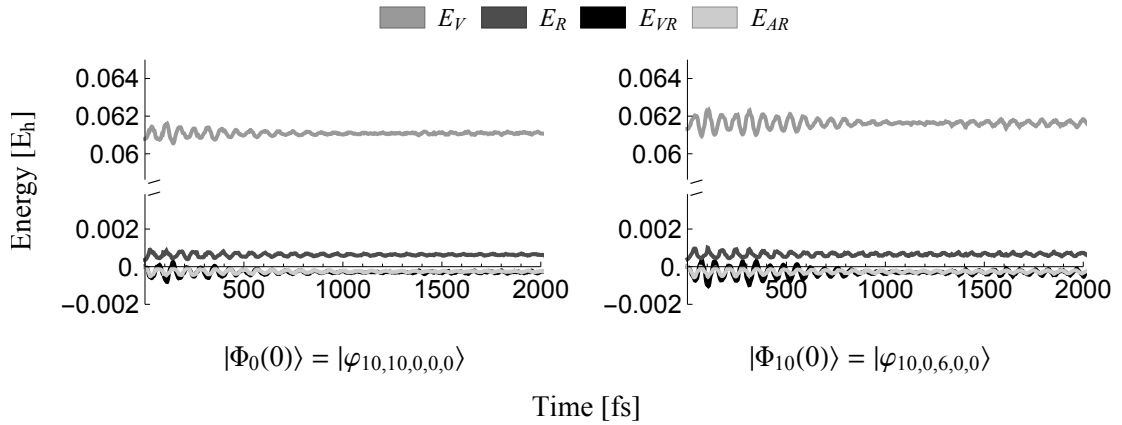


Figure 3:  $\langle E_i \rangle$  for  $i \in \{V, VR, R, AR\}$ , for the temporal evolution of  $|\Phi_{10}(0)\rangle \in \{|\varphi_{10,10,0,0,0}\rangle, |\varphi_{10,0,6,0,0}\rangle\}$ .

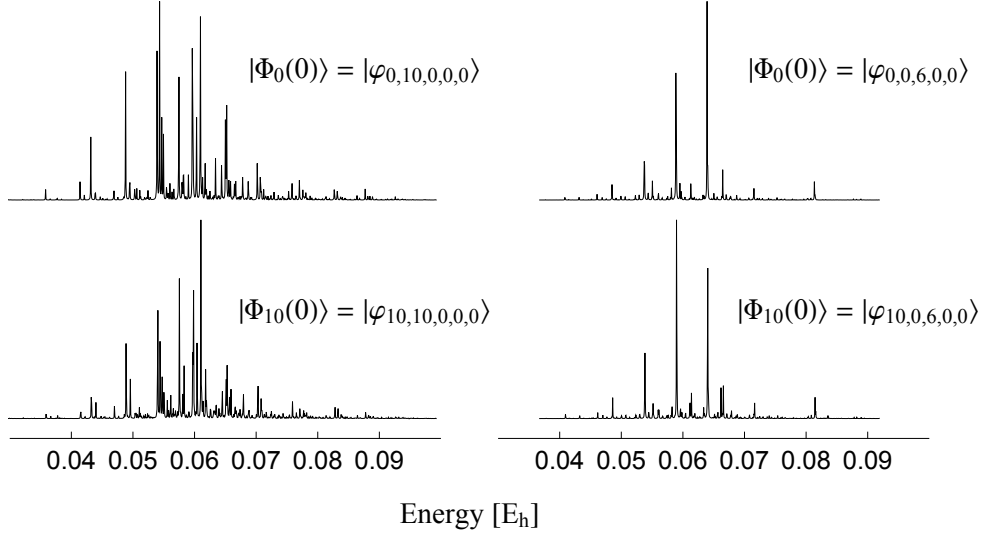


Figure 4:  $\int_{-\infty}^{\infty} \langle \Phi_J(0) | \Phi_J(t) \rangle e^{iEt} dt$  for  $|\Phi_J(0)\rangle \in \{|\varphi_{J,10,0,0,0}\rangle, |\varphi_{J,0,6,0,0}\rangle\}$  with  $J \in \{0, 10\}$ .

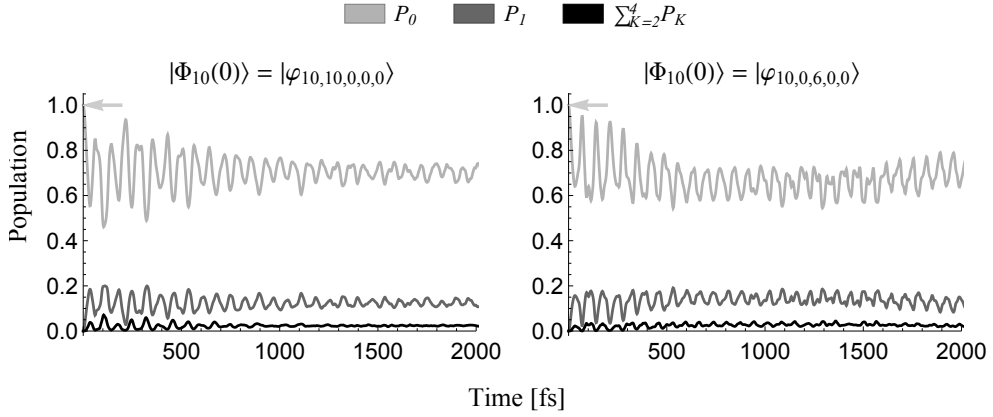


Figure 5:  $P_K(t)$  for  $K \in \{0, 1, 2, 3, 4\}$ , for the temporal evolution of  $|\Phi_{10}(0)\rangle \in \{|\varphi_{10,10,0,0,0}\rangle, |\varphi_{10,0,6,0,0}\rangle\}$  (take into account that  $P_K(t) = P_{-K}(t)$ ).

$\langle E_i \rangle$ , for  $i \in \{CS, OC, \theta K, V, R, VR, AR\}$ , as any expectation value can be written as a sum of cosine functions whose frequencies depend on the energy of the molecular eigenstates composing the wave packet, see Appendix II. Then,  $|\Phi_0(0)\rangle$  and  $|\Phi_J(0)\rangle$  must have an approximately equal molecular eigenstate composition (spectral feature). This can be confirmed by means of the Fourier transform of the autocorrelation function, which is shown in Fig. 4. In this figure, it can be seen that the molecular eigenstate composition for  $|\Phi_{10}(0)\rangle$  is approximately the same as for  $|\Phi_0(0)\rangle$ . When superimposing these spectra,

it is noted that the molecular eigenenergies are energy shifted to slightly higher values for  $|\Phi_{10}(0)\rangle$  with respect to  $|\Phi_0(0)\rangle$ . This indicates an approximately good separation of vibrational and rotational DOF's. Therefore, a  $K$ -mixing mechanism is not expected, which is confirmed by following the evolution of the populations in the  $K$ -manifolds, as shown in Fig. 5.

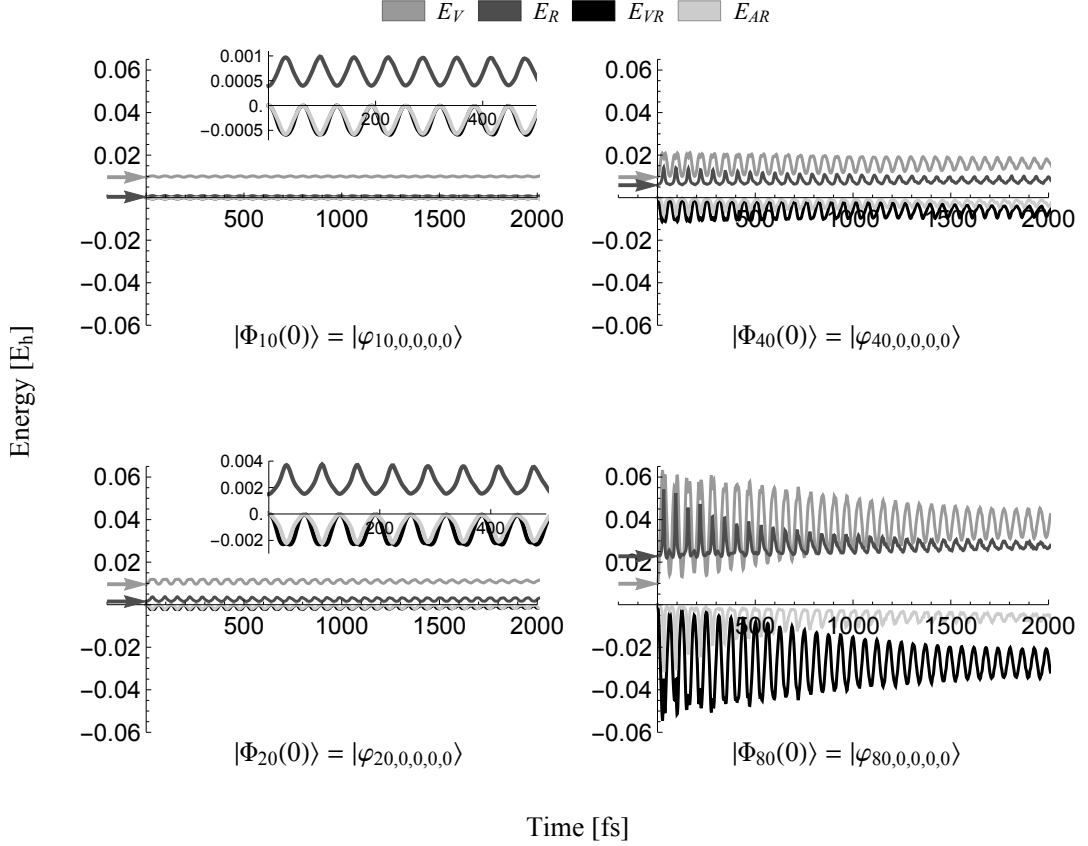


Figure 6:  $\langle E_i \rangle$  for  $i \in \{V, VR, R, AR\}$ , for the temporal evolution of  $|\Phi_J(0)\rangle \in \{|\varphi_{J,0,0,0,0}\rangle\}$  with  $J \in \{10, 20, 40, 80\}$ . Arrows show the initial value of  $\langle E_i \rangle$ , except for  $\langle E_{VR} \rangle$  and  $\langle E_{AR} \rangle$  which are always equal to 0 at  $t=0$ .

Regarding the centrifugal coupling, as the dominant component is mostly  $K=0$  at all times, the coupling responsible for  $K$ -preserving vibrational mixing is mainly  $\hat{A}\hat{J}^2 = \frac{J(J+1)}{2\mu_2 R_2^2}$ . On account of Fig. 2, it can be seen that for  $(n'_{CS}, n'_{OC}) = (11, 0)$  or  $(0, 7)$ ,  $\langle \varphi_{10, n'_{CS}, n'_{OC}, 0, 0} | \frac{1}{2\mu_2 R_2^2} | \varphi_{10, n_{CS}, n_{OC}, 0, 0} \rangle$  is not strong enough to cause IVR. Even though *a priori* we cannot explain why this matrix element is small we can predict that the centrifugal coupling will be enhanced at higher rotational excitations because of the increasing

$J(J+1)$  term. From a different perspective, we can think of  $\hat{A}\hat{J}^2$  as an effective potential, which disturbs the PES, instead of a coupling between different vibrational states. In this way, we can argue that the molecular geometry of the OCS is very “stiff”, i.e., the potential wells in the PES restrict significantly the configurations explored by each DOF. Then, much more rotational energy is required to rotationally “distort” the molecule than just a  $(J, \langle K \rangle) = (10, 0)$  excitation.

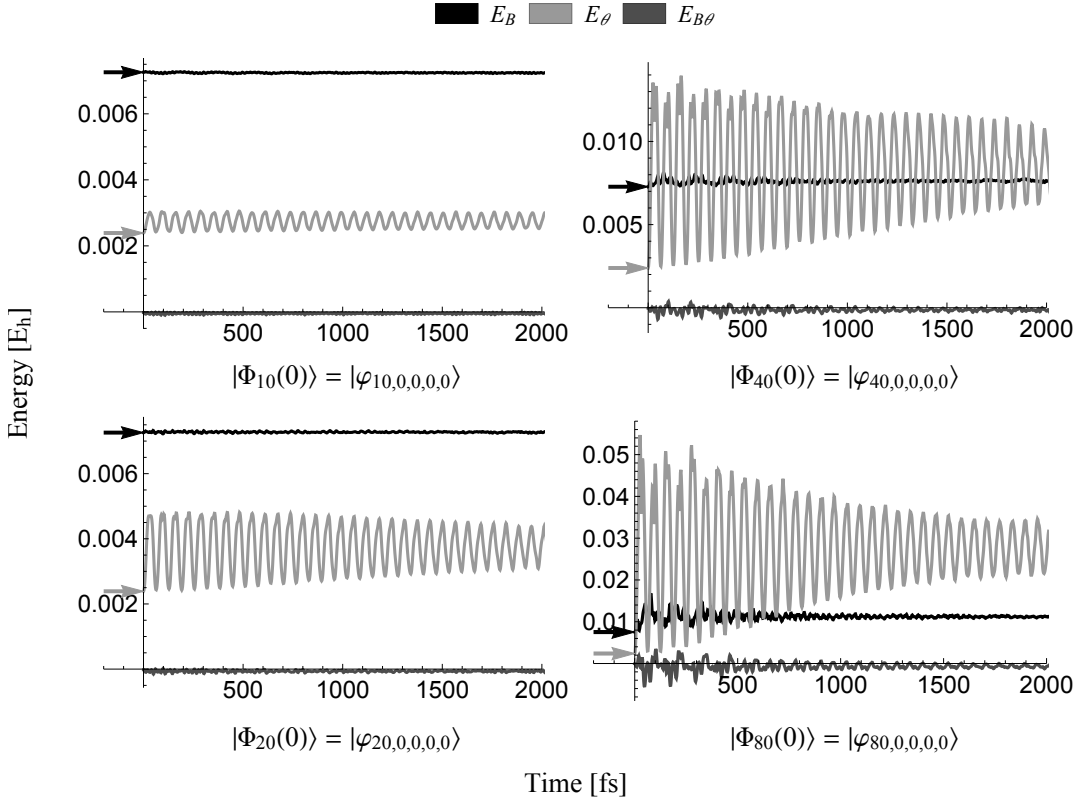


Figure 7:  $\langle E_i \rangle$  for  $i \in \{B, \theta, B\theta\}$ , for the temporal evolution of  $|\Phi_J(0)\rangle \in \{|\varphi_{J,0,0,0}\rangle\}$  with  $J \in \{10, 20, 40, 80\}$ .  $\langle E_{B\theta} \rangle \equiv \langle \Phi_J(t) | (\hat{H}_V - \hat{H}_B - \hat{H}_\theta) | \Phi_J(t) \rangle$ . Arrows show the initial value of  $\langle E_i \rangle$ , except for  $\langle E_{B\theta} \rangle$  which is always equal to 0 at  $t = 0$ .

Now, we examine the evolution of the wave packets  $|\Phi_J(0)\rangle = |\varphi_{J,0,0,0}\rangle$ , with  $J \in \{10, 20, 40, 80\}$ , to give insight on how much rotational energy is necessary to perturb the vibrational energy and possibly the IVR. In Fig. 6, it is appreciated that the variations in the vibrational energy increases relatively little with  $J$ . Therefore, it may be suspected that IVR is not affected by rotational excitations as high as  $J = 40$ . To assess this suspicion,

we split  $\langle E_V \rangle$  into  $\langle E_\theta \rangle$  and  $\langle E_B \rangle = \langle \Phi_J(t) | \hat{H}_B | \Phi_J(t) \rangle$ , where  $\hat{H}_B$  is a two dimensional Hamiltonian including the *CS* and *OC* Hamiltonians and the coupling between them (see Appendix I). The results displayed in Fig. 7 allow us to conclude that even at high rotational energies the *CS* and *OC* modes will not be perturbed significantly, at least for low bond excitations. The perturbation of the vibrational energy is due to the interaction between the  $\theta$  mode and the rotational DOF associated with  $K$ .

### 3.2.2 Bending excitations

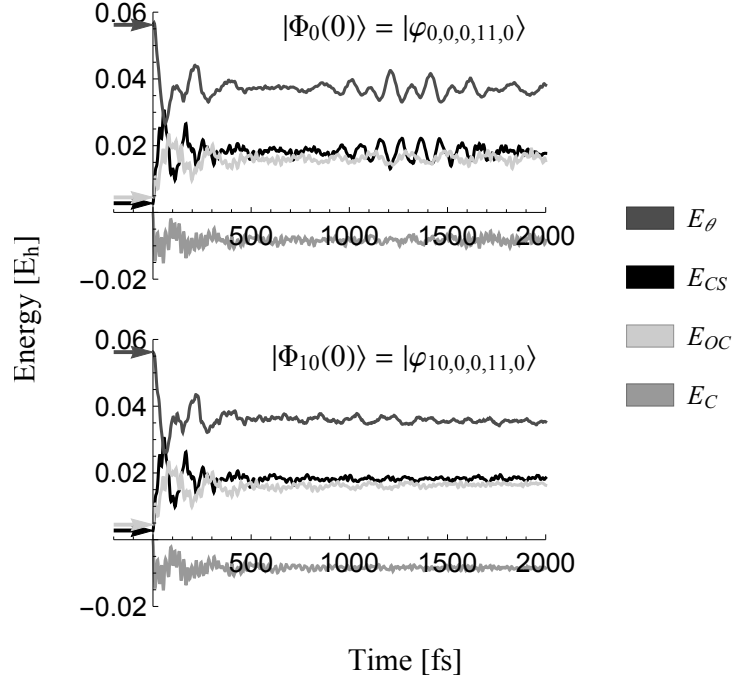


Figure 8:  $\langle E_i \rangle$  for  $i \in \{CS, OC, \theta, C\}$ , for the temporal evolution of  $|\Phi_J(0)\rangle \in \{|\varphi_{0,0,0,11,0}\rangle, |\varphi_{10,0,0,11,0}\rangle\}$ . Arrows show the initial value of  $\langle E_i \rangle$ , except for  $\langle E_C \rangle$  which is always equal to 0 at  $t = 0$ .

With our attention now on the  $\theta$  mode, here we investigate the evolution of the wave packet  $|\Phi_0(0)\rangle = |\varphi_{0,0,0,11,0}\rangle$  vs. the evolution of the wave packet  $|\Phi_{10}(0)\rangle = |\varphi_{10,0,0,11,0}\rangle$ . These wave packets have an energy of about 30% of the dissociation threshold. As can be seen in Fig. 8, now the IVR process is affected, in contrast with the case where the initial excitation is localized in a bond. Namely, the revival of coherent oscillations after about 1000 fs is damped, leaving the system in a steady state, i.e., an apparently

decoherent state. However, the net redistribution is not modified. In Fig. 9 we explore the rotationally-induced vibrational decoherence for lower bending excitations. Clearly, the rotational excitation strongly contributes to decoherence after  $\sim 500$  fs.

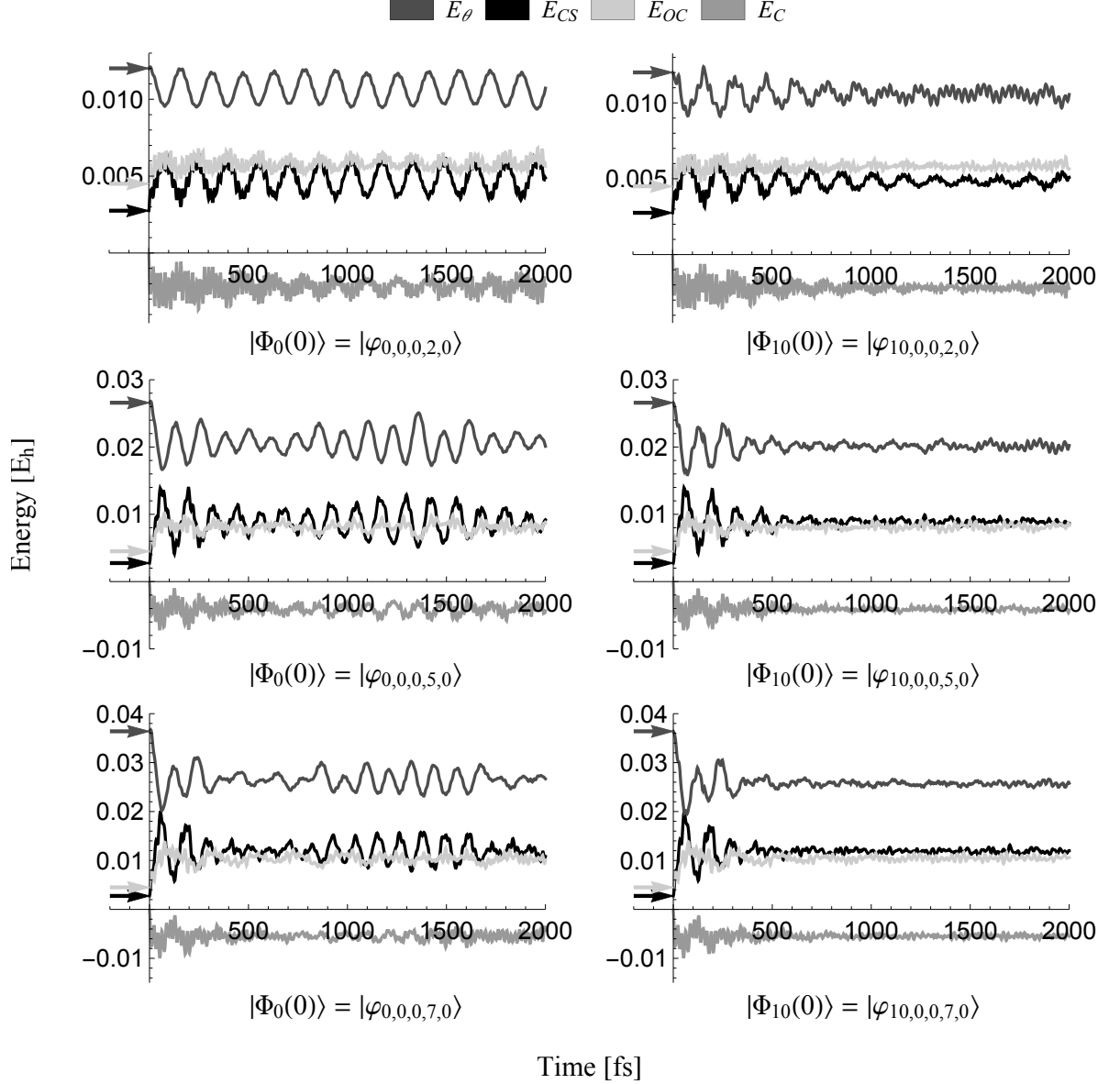


Figure 9:  $\langle E_i \rangle$  for  $i \in \{CS, OC, \theta, C\}$ , for the temporal evolution of  $|\Phi_J(0)\rangle \in \{|\varphi_{0,0,0,n_\theta,0}\rangle, |\varphi_{10,0,0,n_\theta,0}\rangle\}$  with  $n_\theta \in \{2, 5, 7\}$ . These wave packets have an energy of about 9, 15 and 20% of the OCS dissociation energy, respectively. Arrows show the initial value of  $\langle E_i \rangle$ , except for  $\langle E_C \rangle$  which is always equal to 0 at  $t = 0$ .

The vibrational decoherence, apparent in the expectation values, is mediated by new frequencies featuring in the spectral composition of the wave packet with  $J = 10$  not

present in the wavepacket with  $J = 0$ , as shown in Fig. 10. This is related with the loss of goodness of the  $K$  quantum number in excited bending states, as observed in Fig. 11.

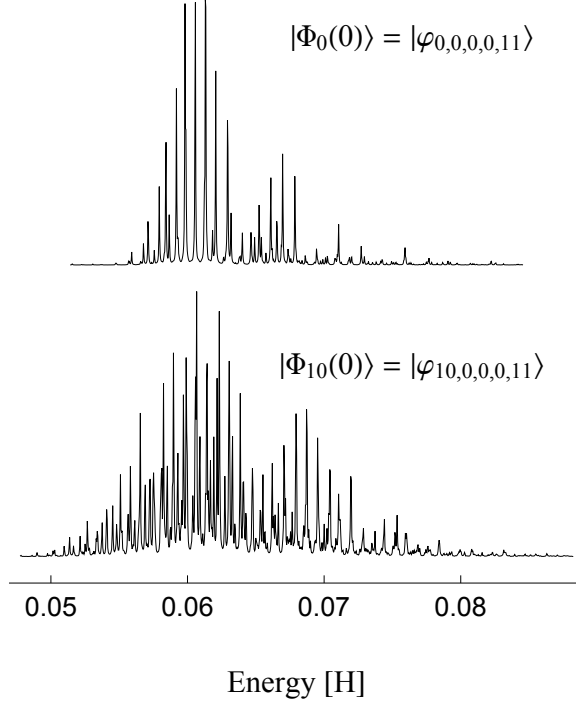


Figure 10:  $\int_{-\infty}^{\infty} \langle \Phi_J(0) | \Phi_J(t) \rangle e^{iEt} dt$  and for  $|\Phi_J(0)\rangle \in \{|\varphi_{0,0,0,11,0}\rangle, |\varphi_{10,0,0,11,0}\rangle\}$ .

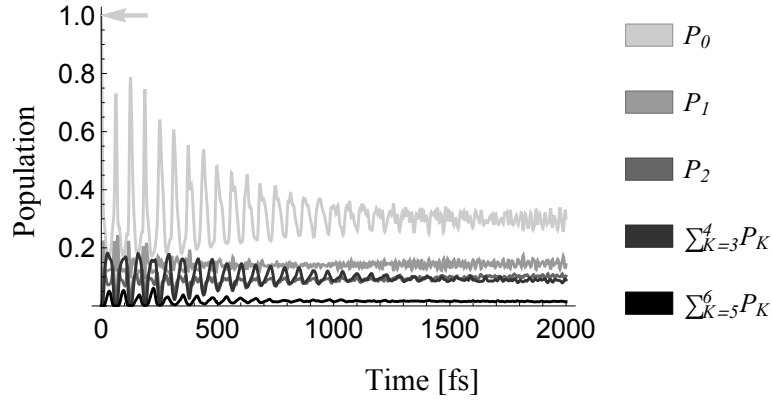


Figure 11:  $P_K(t)$  for  $K \in \{0, 1, \dots, 6\}$ , for the temporal evolution of  $|\Phi_{10}(0)\rangle = |\varphi_{10,0,0,11,0}\rangle$  (take into account that  $P_K(t) = P_{-K}(t)$ ).

Simulations about the dominant mechanism causing  $K$ -mixing, i.e., Coriolis coupling or VIRAS, are currently lacking. But according to the observations in the previous section, when the initial condition is  $K = 0$ , it is probable that both mechanisms contribute

equally to the  $K$ -mixing. But as  $K \neq 0$  states become populated VIRAS could become the dominant term (see Fig. 1). However, more data are needed to reach a conclusion.

We ran simulations without including the Coriolis and asymmetric rotor couplings, obtaining the same results for  $J = 0$  and  $J = 10$ , i.e., evolving  $|\Phi_{10}(0)\rangle$  with a Hamiltonian excluding these couplings gives the results shown in Fig. 8 for  $|\Phi_0(0)\rangle$ . Therefore, centrifugal coupling is not involved in the modification of IVR, as in bond excitation cases.

Interestingly, the IVRET in this case is not significantly different from the bond excitation cases, as a comparison of Figs. 3 and 12 show. Then, the total vibrational energy does not need to change appreciably in order to modify the IVR.

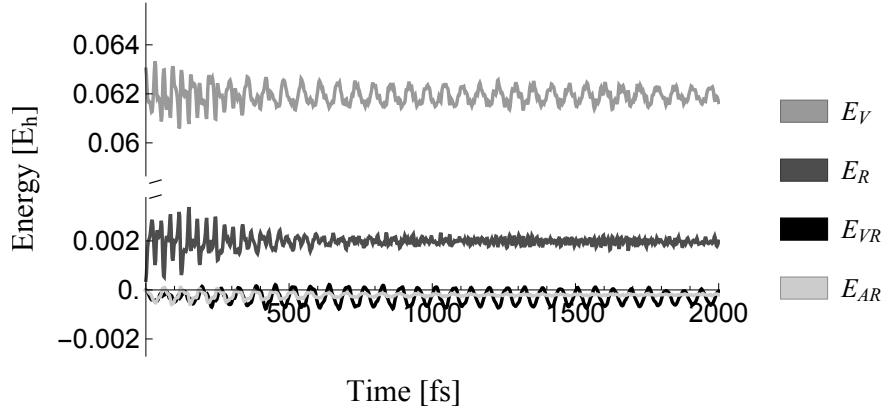


Figure 12:  $\langle E_i \rangle$  for  $i \in \{V, VR, R, AR\}$ , for the temporal evolution of  $|\Phi_{10}(0)\rangle = |\varphi_{10,0,0,11,0}\rangle$ .

## 4 Concluding remarks

We investigated IRVR in an isolated OCS molecule in its electronic ground state to dilucidate possible effects on IVR of low vibrational excitations caused by low rotational excitations. By considering the cases  $J = 0$  and  $J = 10$ , we found that excitations on bonds are not affected by low rotational excitations. But IVR does change if the excited vibration corresponds to the bending mode, in particular a loss of coherence is observed. However, the net redistribution is not altered in the analyzed time scale.

In this rotational excitation regime, we found that centrifugal coupling is absent.  $K$ -mixing was identified as the mechanism which causes decoherence. We did not determine if  $K$ -mixing was predominantly caused by Coriolis coupling or VIRAS, but we provided a discussion showing that likely both mechanisms contribute equally, at least at short times. This conclusion can be applied to any molecule as  $K$ -mixing is due to the same terms, i.e.,  $(\hat{J}_+^{BF} - \hat{J}_-^{BF})$  and  $([\hat{J}_+^{BF}, \hat{J}_z^{BF}]_+ + [\hat{J}_-^{BF}, \hat{J}_z^{BF}]_+)$ .

Therefore, for OCS, modification of IVR upon low rotational excitation is due mainly to  $K$ -mixing and its extent depends on whether the bending mode is excited or not. We cannot provide an explanation why the  $|\varphi_{J,n_{CS},n_{OC},0,0}\rangle \rightarrow \{|\varphi_{J,n'_{CS},n'_{OC},n_\theta,K}\rangle\}$  pathways are blocked in comparison with the  $|\varphi_{J,n_{CS},n_{OC},n_\theta \neq 0,0}\rangle \rightarrow \{|\varphi_{J,n'_{CS},n'_{OC},n'_\theta,K}\rangle\}$  pathways. However, we believe this is directly related with the inherent non-separability of the bending mode and the rotation around the BF-frame  $z$ -axis.

On account of the strong coupling between these two DOF's, we think we can extend these conclusions to linear triatomic molecules in general. As a contrasting example to OCS, we ran analogous simulations for the lithium hydroxide molecule (LiOH), which is quasi-linear and possesses a non-rigid bending DOF, reaching the same conclusions as for OCS.

## A Appendix I

The KEO for a three-body system in valence coordinates ( $R_1$ ,  $R_2$  and  $\theta$ ) and Euler angles embedded in a ZZ<sup>I</sup>X BF-frame has been already reported <sup>[112–115]</sup>, see Fig. 13 for definition of the BF-frame. Here we show the Hamiltonian split into:  $\hat{H} = \hat{H}_V + \hat{H}_R + \hat{H}_{VR} + \hat{H}_{AR}$ . The subscripts 1 and 2 correspond to *OC* and *CS*, respectively.

$$\begin{aligned} \hat{H}_V = & -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2} - \frac{\cos \theta}{m_C} \frac{\partial^2}{\partial R_1 \partial R_2} + \frac{1}{m_C} \left( \frac{1}{R_2} \frac{\partial}{\partial R_1} + \frac{1}{R_1} \frac{\partial}{\partial R_2} \right) \frac{\partial}{\partial \theta} \sin \theta \\ & + \frac{1}{2m_C R_1 R_2} \left( \cos \theta \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \cos \theta \right) \\ & - \left( \frac{1}{2\mu_1 R_1^2} + \frac{1}{2\mu_2 R_2^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + V(R_1, R_2, \theta), \end{aligned} \quad (\text{A.1})$$

$$\begin{aligned} \hat{H}_{VR} = & \left[ -\frac{\sin \theta}{2m_C R_2} \frac{\partial}{\partial R_1} - \frac{1}{4m_C R_1 R_2} \left( \cot \theta \frac{\partial}{\partial \theta} \sin \theta + \frac{\partial}{\partial \theta} \sin \theta \cot \theta \right) \right. \\ & \left. + \frac{1}{4\mu_2 R_2^2} \left( \frac{\partial}{\partial \theta} \sin \theta \frac{1}{\sin \theta} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \right) \right] \left( \hat{J}_+^{BF} - \hat{J}_-^{BF} \right), \end{aligned} \quad (\text{A.2})$$

$$\hat{H}_R = \frac{1}{2\mu_2 R_2^2} \hat{J}^2 - \left[ \frac{\cot \theta \csc \theta}{m_C R_1 R_2} - \csc^2 \theta \left( \frac{1}{2\mu_1 R_1^2} + \frac{1}{2\mu_2 R_2^2} \right) + \frac{1}{\mu_2 R_2^2} \right] \left( \hat{J}_z^2 \right)^{BF}, \quad (\text{A.3})$$

$$\hat{H}_{AR} = \frac{1}{4} \left( \frac{\cot \theta}{\mu_2 R_2^2} - \frac{\csc \theta}{m_C R_1 R_2} \right) \left[ \left[ \hat{J}_+^{BF}, \hat{J}_z^{BF} \right]_+ + \left[ \hat{J}_-^{BF}, \hat{J}_z^{BF} \right]_+ \right]. \quad (\text{A.4})$$

Here, it is not necessary to express the angular momentum operators in terms of the Euler angles, for an explicit expressions see Ref. [116].  $\mu_i$  is the reduced mass corresponding to bond  $i$ ,  $m_C$  is the carbon mass and  $V(R_1, R_2, \theta)$  is the PES reported in Ref. [105].

The zero-order vibrational Hamiltonians are defined as:

$$\hat{H}_i = -\frac{1}{2\mu_i} \frac{\partial^2}{\partial R_i^2} + V(R_i, R_{j \neq i, e}, \theta_e), \quad i, j \in \{1, 2\}, \quad (\text{A.5})$$

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<sup>I</sup>Also known as bond-Z BF-frame.

$$\begin{aligned}
\hat{H}_{\theta K} = & \left( \frac{1}{2\mu_1 R_{1,e}^2} + \frac{1}{2\mu_2 R_{2,e}^2} \right) \left( -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \csc^2 \theta \left( \hat{J}_z^2 \right)^{BF} \right) \\
& - \frac{1}{2m_C R_{1,e} R_{2,e}} \left[ \cos \theta \left( -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \csc^2 \theta \left( \hat{J}_z^2 \right)^{BF} \right) \right. \\
& \left. + \left( -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \csc^2 \theta \left( \hat{J}_z^2 \right)^{BF} \right) \cos \theta \right] + V(R_{1,e}, R_{2,e}, \theta), \quad (\text{A.6})
\end{aligned}$$

where the subscript  $e$  in the coordinates refers to equilibrium values. In the text we also refer to  $\hat{H}_B$ , which is defined as

$$\hat{H}_B = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{\cos \theta_e}{m_C} \frac{\partial^2}{\partial R_1 R_2} + V(R_1, R_2, \theta_e). \quad (\text{A.7})$$

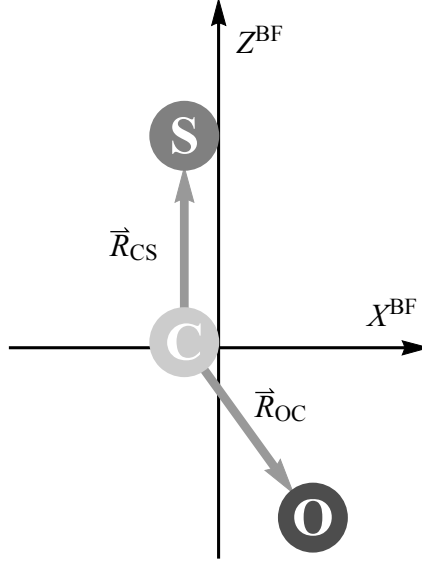


Figure 13: BF-frame embedding. In this ZZX frame, the  $z$ -axis is parallel to  $\vec{R}_{CS}$  and  $\vec{R}_{OC}$  is always pointing towards the positive  $x$ -axis.  $\vec{R}_i \cdot \vec{R}_i = R_i^2$  for  $i \in \{CS, OC\}$  and  $\vec{R}_{CS} \cdot \vec{R}_{OC} = R_{OC} R_{CS} \cos \theta$ .  $\vec{R}_{CS}$  and  $\vec{R}_{OC}$  have no component on the  $y$ -axis.

## B Appendix II

The expansion of a wave packet  $|\Upsilon(t)\rangle$  in the molecular eigenstate basis set reads

$$|\Upsilon(t)\rangle = \sum_{n=0}^{n_f} c_n e^{-iE_n t} |\psi_n\rangle + \int_{n_f+dn}^{\infty} c_n e^{-iE_n t} |\psi_n\rangle dn. \quad (\text{B.1})$$

Then, the expectation value of any Hermitian operator,  $\hat{O}$ , can be written as

$$\begin{aligned} \langle O \rangle &\equiv \langle \Upsilon(t) | \hat{O} | \Upsilon(t) \rangle \\ &= \sum_{l=0}^{l_f} |a_l|^2 O_l + \int_{l_f+dl}^{\infty} |a_l|^2 O_l dl + \sum_{l>l',l'}^{l_f,l_f} B_{ll'} \cos(\omega_{ll'} t + \delta_{ll'}) \\ &\quad + \int_{l_f+dl}^{\infty} \int_{l_f+dl}^l B_{ll'} \cos(\omega_{ll'} t + \delta_{ll'}) dl' dl + \int_{l_f+dl}^{\infty} \sum_{l'=0}^{l_f} B_{ll'} \cos(\omega_{ll'} t + \delta_{ll'}) dl \end{aligned} \quad (\text{B.2})$$

where

$$\begin{aligned} \omega_{ll'} &\equiv E_l - E_{l'}, & O_{ll'} &\equiv \langle \psi_l | \hat{O} | \psi_{l'} \rangle, & A_{ll'} &\equiv a_l^* a_{l'} O_{ll'}, \\ B_{ll'} &\equiv 2 |A_{ll'}|, & \delta_{ll'} &\equiv \frac{\pi}{2} - \arctan \frac{\text{Re}\{A_{ll'}\}}{\text{Im}\{A_{ll'}\}}. \end{aligned}$$

For the wave packets used in this research:

$$\langle O \rangle = \sum_{l=0}^{l_f} |a_l|^2 O_l + \sum_{l>l',l'}^{l_f,l_f} B_{ll'} \cos(\omega_{ll'} t + \delta_{ll'}). \quad (\text{B.3})$$

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