Rovibrational spectra of diatomic molecules in strong electric fields

R González-Férez$^{1,2}$ and P Schmelcher$^{2,3}$

$^1$Departamento de Física Moderna & Instituto “Carlos I” de Física Teórica y Computacional, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain
$^2$Theoretische Chemie, Physikalisch-Chemisches Institut, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany
$^3$Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, D-69120 Heidelberg, Germany

E-mail: rogonzal@ugr.es, Peter.Schmelcher@pci.uni-heidelberg.de

Abstract. We investigate the effects of a strong static electric field on the rovibrational spectra of diatomic heteronuclear molecules in a $^1\Sigma^+$ electronic ground state. Using a hybrid computational technique combining discretization and basis set methods the full rovibrational equation of motion is solved. As a prototype for our computations we take the carbon monoxide molecule. For experimentally accessible field strengths we observe that while low-lying states are not significantly affected by the field, for highly excited states strong orientation and hybridization are achieved. We propose an effective rotor Hamiltonian, including the main properties of each vibrational state, to describe the influence of the electric field on the rovibrational spectra of a molecular system with a small coupling between its rotational and vibrational motions. This effective rotor approach goes significantly beyond the rigid rotor approach and is able to describe the effect of the electric field for highly excited states.

1. Introduction

Historically one motivation to study the effects of electric fields on the molecular motion was the possibility of orienting or aligning molecules in order to obtain a deeper understanding and control of chemical reactions. Nowadays, cooling, trapping, guiding and manipulating atoms and molecules is done by applying external fields. Even more, a molecular condensate [1] will give rise to new applications in ultracold molecular physics or in molecular optics, such as ultrahigh resolution and high precision spectroscopy of molecules, collisions of ultracold molecular physics, and possible state-selective chemical reactions [2–4]. External fields play a key role in the control of cold molecular systems and in particular in the molecular rotational and vibrational dynamics. However, little is known about how the highly excited rovibrational dynamics of molecules is affected by electric fields.

Traditionally, the theoretical description of the effect of an electric field in a diatomic molecular system was done by means of the rigid rotator approximation, neglecting the coupling of the rotational and vibrational motions and assuming a fixed permanent dipole moment of the molecule. The rigid rotor Hamiltonian for diatomic molecules given by the expression,

$$\mathcal{H} = \frac{J^2}{2\mu R_{eq}^2} - FD_{eq}\cos \theta$$

(1)

where $R_{eq}$ and $D_{eq}$ are the equilibrium internuclear distance and the corresponding dipole moment, $J$ is the angular momentum, $\theta$ is the angle between the molecular axis and the external field and $\mu$ is...
the reduced mass of the nuclei. This Hamiltonian is integrable, and it was studied at the beginning of
the seventies by K. von Meyenn [5]. Although there was a huge amount of studies of molecules in
inhomogeneous [6, 7] and homogeneous electric field, in magnetic fields [8] and in laser fields [9], there
is a lack of more realistic descriptions of the problem.

In this work we go beyond the above approximation and provide a more realistic description of the
system by including the rotation-vibration coupling and the dependence of the dipole moment on the
vibrational coordinate. We will analyze the effect of an electric field in the rovibrational dynamic of
heteronuclear diatomic molecules, in a electronic ground state with $^1\Sigma^+$ symmetry. The regime of field
strength of interest is such that it strongly influences the heavy particle dynamics of the molecule, which
is described by a nonperturbative approach, but does not yet lead to significant electronic ionization,
described by perturbation theory. As an example of application the carbon monoxide molecule is used.
We propose an "effective rotor Hamiltonian" to describe the effect of an electric field on the rovibrational
spectrum of diatomic molecules in general with different energy scales for the rotational and vibrational
motions [10].

2. Hamiltonian and computational method

In the framework of the Born-Oppenheimer approximation, the Hamiltonian of a diatomic molecule,
in a $^1\Sigma^+$ electronic ground state, exposed to an external homogeneous static electric field in a rotating
molecule fixed frame with the origin at the center of mass of the nuclei, takes the form:

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{\mathbf{J}^2(\theta, \phi)}{2\mu R^2} + \epsilon(R) - F D(R) \cos \theta$$

where $R$ and $\theta, \phi$ are the internuclear coordinate and Euler angles, respectively. $\mathbf{J}(\theta, \phi)$ is the orbital
angular momentum, $\epsilon(R)$ represents the field-free electronic potential energy curve (PEC) and $D(R)$ is
the electronic dipole moment function (EDMF). In the field-free case each state is characterized
by its vibrational $\nu$, rotational $J$ and magnetic $M$ quantum numbers. In the presence of an external
electric field only the magnetic quantum number $M$ is conserved, giving rise to a non-integrable two-
dimensional Schrödinger equation in $(R, \theta)$-space. In order to solve this rovibrational equation of motion
we developed a hybrid computational approach. For the angular part a basis set expansion in terms of
Legendre functions is used. The vibrational degree of freedom is treated by a radial harmonic oscillator
discrete variable representation. Employing the variational principle, the initial differential equation is
finally reduced to a symmetric eigenvalue problem which is diagonalized with the help of Krylov type
techniques.

3. Results

In this section we present a selection of the results obtained for carbon monoxide, in particular the
expectation values $\langle \cos \theta \rangle$ and $\langle J^2 \rangle$ will be discussed. Figure 1 shows the PEC and EDMF for the
electronic ground state of the CO molecule as a function of the vibrational coordinate $R$. The EDMF is
negative and of small absolute value at the equilibrium internuclear distance $R_{eq}$. With increasing $R$ there
is a sign change and a maximum follows for an internuclear distance much larger than $R_{eq}$. We expect
that the influence of the electric field will be more pronounced for high lying excited states compared to
the low lying states.

Figure 2a illustrates the behavior of the expectation value $\langle \cos \theta \rangle$ of the states with spherical
symmetry in the field-free case as a function of the degree of excitation $\nu$ for the field strengths $F = 10^{-6}, 5 \cdot 10^{-6}, 10^{-5}, 5 \cdot 10^{-5},$ and $10^{-4}$ a.u.. $\langle \cos \theta \rangle$ provides a measure of the orientation of the state along the field direction, the closer its absolute value is to one, the stronger is the orientation of the state along the field. Due to the field-free spherical symmetry of the states we have $\langle \cos \theta \rangle = 0$ for $F = 0$. For the lowest field strength, $F = 10^{-6}$ a.u., the response to the electric field is rather weak, being negligible for the low-lying levels. While for $F = 10^{-4}$ a.u. states with field-free $\nu > 50$, already show
a significant orientation $0 < \theta \lesssim 40^\circ$. For all field strengths considered $\langle \cos \theta \rangle$ monotonically increases with increasing degree of excitation reaching a maximum for the state $\nu = 68$, and decreases thereafter. Only for the states $\nu \leq 4$ $\langle \cos \theta \rangle$ is negative, they are oriented opposite to the field direction, while the rest of the spectra is along the field direction. This change of sign reflects the change of the sign that the EDMF of the CO molecule exhibits for $R > R_{eq}$.

Figure 2b shows the expectation value $\langle J^2 \rangle$ of states possessing a field-free spherical symmetry as a function of the vibrational label $\nu$ for $F = 5 \cdot 10^{-6}, 10^{-5}, 5 \cdot 10^{-5}$, and $10^{-4}$ a.u. $\langle J^2 \rangle$ provides a measure of the hybridization of the rotational motion for $F = 0$. The effects due to the electric field depend not only on the field strength but also strongly on the degree of excitation. For all field strengths $\langle J^2 \rangle$ passes through a minimum for the state with $\nu = 4$ where the influence of the external field is almost negligible. With further increasing $\nu$ the mixing of states becomes more pronounced and $\langle J^2 \rangle$ monotonically increases up to the maximum for $\nu = 68$, for which $\langle R \rangle \approx 4.6$ a.u.. Generally for $\nu \lesssim 10$ the mixture of $F = 0$ rotational states is very minor for all field strengths. The range of $J$ values contributing to each state becomes significantly larger as the field strength increases.

4. The adiabatic approximation

In this section we propose an effective rotor approximation to describe the effect of an electric field on those molecules and states for which the energy scales associated with the rotational and vibrational motions differ by several orders of magnitude. Taking into account that the magnetic quantum number is conserved the rovibrational Hamiltonian in an electric field (2) is written as follows in term of the
canononical pairs
\[ H = \frac{1}{2\mu} \left[ P_R^2 + \frac{1}{R^2} P_\theta^2 \right] + \epsilon(R) - FD(R) \cos \theta, \]
with \( P_R \) and \( P_\theta \) being the conjugate momenta belonging to the vibrational coordinate \( R \) and Euler angle \( \theta \). For simplicity only \( M=0 \) states are considered.

Let us assume that the vibrational problem has been solved for a specific value of the rotational coordinate \( \theta \) assuming \( P_\theta \to 0 \), \( (P_\theta = \mu R^2 \dot{\theta}) \),
\[ \left[ \frac{1}{2\mu} P_R^2 + \epsilon(R) - FD(R) \cos \theta \right] \psi_v(R; \theta) = E_v(\theta) \psi_v(R; \theta) \]
where \( \psi_v(R; \theta) \) is a member of an orthonormal basis set and depends parametrically on the angle \( \theta \). We propose the following ansatz for the rovibrational wavefunction
\[ \Psi(R, \theta) = \sum_v \psi_v(R; \theta) \chi_v(\theta), \]
and assume that (for certain molecules) the influence of the electric field on the vibrational dynamics is very small, and can therefore be described by perturbation theory. Thus performing an adiabatic separation of the rotational and vibrational motions we arrive at the following “effective rotor Hamiltonian”
\[ H_v^R = \frac{1}{2\mu} \left( R^{-2} \right)^{(0)} \hat{J}^2 - F \cos \theta \left( D(R) \right)^{(0)} + E_v^{(0)} \]
with \( \left( R^{-2} \right)^{(0)} = \langle \psi_v^{(0)} | R^{-2} | \psi_v^{(0)} \rangle \) and \( \left( D(R) \right)^{(0)} = \langle \psi_v^{(0)} | D(R) | \psi_v^{(0)} \rangle \), \( E_v^{(0)} \) and \( E_v^{(0)} \) being the field-free rovibrational wavefunction and energy respectively. Where the first term is an effective rotational kinetic energy, the second one represents the interaction with the electric field through an effective electric dipole moment \( \langle D(R) \rangle^{(0)} \), and the last one is just a shift of the energy. It looks different for each vibrational state and therefore describes an effective vibrational state-dependent angular motion. Indeed it is able to describe highly excited states in an electric field, whereas the traditional rigid rotor Hamiltonian (1) can not do so.

In order to check the validity of the adiabatic rotor scheme we have compared it with the full rovibrational description by means of the relative difference \( \Delta A_v = \frac{\left| A_v^R - A_v^F \right|}{A_v^F} \) where \( A_v^F \) represents \( \langle \cos \theta \rangle_{\psi_v}^{F(R)} \) or \( \left\langle J^2 \right\rangle_{\psi_v}^{F(R)} \), \( F \) indicates that they have been computed in the framework of the full rovibrational description and \( R \) refers to the effective rotor approach. Figure 3 illustrates the relative differences of these expectation values as a function of the vibrational number of the states for \( F = 10^{-4} \) a.u. Except for the state with \( v = 4 \) for \( \langle \cos \theta \rangle \) and the states with \( v = 4 \) and \( 5 \) for \( \langle J^2 \rangle \), we always obtain \( \Delta A_v < 0.001 \). We conclude that the effective rotor approach provides an excellent description of the influence of an electric field on the rovibrational spectrum of the CO molecule for the states considered here. This is by no means restricted to the CO molecule but expected to hold for a broad variety of molecules.

5. Conclusions
An effective rotor Hamiltonian is derived that describes the influence of the external field on a diatomic molecule, with a minor coupling between the vibrational and rotational motions. By the introduction of main properties of each vibrational state it can describe the effect of the field for the complete spectrum, and it is superior to the traditional rigid rotator approximation. Its validity was demonstrated for the CO molecule by comparison with the full rovibrational results [10]. However, it is expected to be a good approximation for many heteronuclear diatomics.

The vibrational state-dependence of the effective rotor equation opens new perspectives for the application of the external field to obtain hybridization, alignment and orientation of the rotational
motion. Moreover going to electronically excited states still enriches these possibilities of obtaining new field-dressed properties throughout the rovibrational spectra. Obviously it might be possible to selectively control chemical reaction dynamics, influence scattering inelastic cross sections or control the dissociation dynamics, also to use these states in cold molecular physics, via the preparation of the molecule in a highly oriented and hybridized rovibrational state.

It remains to study the validity of this effective rotor approach for the part of the spectrum where the rotation-vibration coupling will become increasingly more important, such as states with higher $J$-values for $F = 0$. Even more important and interesting are the floppy molecules that possess a significant rotation-vibration mixing in the absence of the field. Little is known about how they will be affected by an electric field. Typical examples might be the heteronuclear alkali dimers which are of major interest with respect to the formation of ultracold molecular quantum gases.

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