

Rovibrational spectra of diatomic molecules in strong electric fields: The adiabatic regimeR. González-Férez^{1,*} and P. Schmelcher^{1,2,†}¹*Theoretische Chemie, Physikalisch-Chemisches Institut, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany*²*Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, 69120 Heidelberg, Germany*

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We investigate the effects of a strong 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 specific example, the rovibrational spectrum and properties of the carbon monoxide molecule are analyzed for experimentally accessible field strengths. Results for energy levels, expectation values, and rovibrational spectral transitions are presented. They indicate 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 an electric field on the rovibrational spectra of a molecular system with a small coupling between its rotational and vibrational motions. The validity of this approach is illustrated by comparison with the results obtained with the fully coupled rovibrational Schrödinger equation. We thereby demonstrate that it is possible to create state-dependent hybridization of a molecular system, which is of importance for vibrational state-selective chemical reactions. This state dependence is individually different for each molecular system and represents therefore a characteristic feature of the species.

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I. INTRODUCTION

During the past decade a variety of experimental techniques have been developed in order to cool and trap neutral atoms. Using combinations of, e.g., laser and evaporative cooling mechanisms the translational motion of atoms can be slowed down to a few cm/s, which corresponds to typical temperatures on the nanokelvin scale. The motion of the atoms can then be controlled using external fields that provide a suitable trapping potential (e.g., a magneto-optical trap). Since the atoms are isolated from the environment, the trap represents an ideal laboratory to study the physics of a well-defined ensemble of interacting atoms, their number possibly ranging from a few to typically many millions. Due to their complicated level structure the laser cooling approach cannot be applied to provide ultracold molecules. To nevertheless arrive at ensembles of ultracold molecules the following paths are currently pursued. The first one is photoassociation [1–3] of two laser cooled atoms that provides translationally cold molecules in certain well-defined (typically highly excited) vibrational states. A major experimental challenge is to prepare molecules also in well-defined rotational states. In a second experimental setup, an array of time varying inhomogeneous electric fields has been used to decelerate and trap polar molecules [4,5], providing a technique that can be used for a large variety of neutral molecules as a first step in the cooling processes. Finally, the combination of elastic collisions with a cold buffer gas, such as, e.g., helium, with magnetic traps provide an efficient loading technique to cool and trap a large number of paramagnetic molecules [6]. Moreover, it is expected that these already trapped and cooled

molecules could be further cooled by an efficient implementation of, e.g., evaporative cooling.

The prospect of obtaining a Bose-Einstein condensate (BEC) of molecules has become one of the major objectives in BEC physics. An analysis of the vibrational and rotational states of the molecules involved is essential to pave the way toward preparation of a molecular condensate. Beyond this, and due to the interaction between the permanent electric dipole moments of polar molecules, a rich variety of physical phenomena have to be expected in cold dipolar gases, including both spectroscopic and collisional physics [7–9]. Molecular condensates will give rise to applications in areas as diverse as ultracold molecular physics, molecular optics, and potentially also in quantum computing [10]; in particular, cooling and trapping of molecules opens the way to ultrahigh-resolution and high-precision spectroscopy of molecules, to state-selected chemical reactions, to collisions of ultracold molecules, and to study of collective quantum effects in molecular systems.

In this context the influence of external fields on molecules is of utmost importance: cooling, trapping, guiding, and manipulating atoms and molecules is done by applying suitable electric, magnetic, or electromagnetic fields. Even more, external fields play a key role in the control of molecular rotational and vibrational dynamics. However, little is known about how the rovibrational dynamics of molecules is affected by electric fields. Since several of these experimental techniques proceed via highly excited rovibrational states, especial interest arises in the properties of high excitations exposed to the field.

Historically, one motivation to study the effects of electric fields on the molecular motion was the possibility of orienting or aligning molecular systems in fields. Since the chemical reaction dynamics strongly depends on the mutual orientation of the molecules approaching each other, the

*Electronic address: Rosario.Gonzalez@pci.uni-heidelberg.de

†Electronic address: Peter.Schmelcher@pci.uni-heidelberg.de

possibility of defining and changing their orientation is a major step toward a deeper understanding and control of chemical reactions. Molecular orientation has a rich history during which inhomogeneous [11,12] and homogeneous [13–18] electric fields, as well as homogeneous magnetic fields [19,20] and more recently laser fields [21–25] have been applied.

In all the above theoretical descriptions of the response of a molecule to an external field the coupling of the rotational and vibrational motions was neglected and the rigid rotor approximation was employed, assuming a fixed permanent dipole moment of the molecule. The resulting “pendular Hamiltonian” for diatomic molecules is integrable. The effect of an electric field on a rigid rotator was studied at the beginning of the seventies by von Meyenn [26]. Later on this analysis was extended to describe nonpolar molecules [15]. The term “pendular states” characterizes the influence of the electric field on the rotational motion of the molecule: with increasing field strength it becomes a librating one which leads to the orientation of the molecular axis. Each pendular state is a coherent superposition of field-free rotational states. Except for Ref. [27], where the authors investigate the pendular motion of the HCCF molecule in a particular excited vibrational state, the rotation of molecules has exclusively been discussed for low vibrational excitations.

The present work goes beyond these approximations and aims at a more realistic approach to the rovibrational motion in molecules in an external homogeneous electric field. In particular, we include the rotation-vibration coupling and the dependence of the dipole moment on the vibrational coordinates. Especially for highly excited rovibrational states, the additional interactions will have a strong impact on the spectrum and the properties of the systems. Consequently, additional phenomena and effects have to be expected. Effects of weak electric fields on molecular spectra were already investigated very early in the past century. The latter are not the focus of this analysis. We address the situation of strong electric fields for which the intramolecular and field interactions are of comparable strength, thereby excluding a perturbation theory treatment. The field strength regime of interest is such that it strongly influences the heavy particle dynamics of the molecule but does not yet lead to significant ionization. Since the energy scales associated with the motion of the heavy and light particles are typically separated by orders of magnitude there is a wide range of field strengths for which these requirements are met.

The aim of this work is to perform theoretical investigations on the rovibrational dynamics of diatomic molecules, with electronic ground states of $^1\Sigma^+$ symmetry, in strong electric fields. In view of the experimental progress a thorough theoretical understanding of the molecular dynamics in strong electric fields is of utmost importance. With the help of a hybrid computational approach the rovibrational equation of motion for a diatomic molecule in an electric field is solved. The effect of increasing field strength on the energy levels, the expectation values $\langle \cos \theta \rangle$ and $\langle J^2 \rangle$, and the dipole strength of rovibrational spectral transitions will be presented. We will restrict ourselves here to the states evolving from spherically symmetric states in $F=0$. Vibrationally

highly excited but rotationally low-lying excited states will be explored. As an example we will focus on the carbon monoxide molecule. In particular, we will show that the effect of an electric field on diatomic molecules with different energy scales for the rotational and vibrational motions can be described by means of an “effective rotor Hamiltonian.” This Hamiltonian includes the main characteristics of each vibrational level and describes with a high accuracy not only the low-lying states, but in addition the complete rovibrational structure of levels, especially highly excited vibrational states. This approximation predicts which rovibrational states are going to be most affected by the field. One of the main applications of our results is the possibility of achieving state-dependent hybridization, which is an important step toward state-selective chemistry, i.e., the control and manipulation of chemical reactions.

The paper is organized as follows. In Sec. II we define our rovibrational Hamiltonian and briefly discuss some specifics of our computational method. In Sec. III we describe the potential energy curve and electric dipole moment function of a diatomic heteronuclear molecule. Section IV contains the results and the corresponding discussion, including a selection of the results for energy levels, expectation values, and rovibrational spectral transitions. In Sec. V we present the key steps of the adiabatic separation of the vibrational and rotational motions in order to get the effective rotor Hamiltonian. In Sec. VI we compare our results obtained by the fully coupled rovibrational Schrödinger equation with those following the effective rotor approach. The conclusions and outlook are provided in Sec. VII.

II. ROVIBRATIONAL HAMILTONIAN AND COMPUTATIONAL METHOD

A complete description of the dynamics of a molecule in an electric field should include not only the kinetic energy of the electrons and nuclei, the Coulomb and electric field interactions, but also relativistic corrections such as spin-orbit, spin-spin, or hyperfine coupling terms. For spin singlet electronic states possessing a vanishing orbital angular momentum, these interactions are of minor relevance and can be neglected. Then, the Hamiltonian for a diatomic molecule in an external electric field in the laboratory frame reads as

$$H = \sum_{\alpha=1,2} \frac{1}{2M_{\alpha}} \mathbf{p}_{\alpha}^2 + \sum_{i=1}^{N_e} \frac{1}{2m_e} \mathbf{p}_i^2 + V(\mathbf{r}_i, \mathbf{r}_{\alpha}) + V_F(\mathbf{r}_i, \mathbf{r}_{\alpha}),$$

where the first and second terms are the kinetic energy of the nuclei and the electrons, respectively. M_{α} and m_e are the mass of the α th nucleus and of the electron, respectively. $V(\mathbf{r}_i, \mathbf{r}_{\alpha})$ contains all Coulomb interactions. The interaction with the electric field \mathbf{F} is given in the dipole approximation as

$$V_F(\mathbf{r}_i, \mathbf{r}_{\alpha}) = -e\mathbf{F} \cdot \left(\sum_{i=1}^{N_e} \mathbf{r}_i - \sum_{\alpha=1,2} Z_{\alpha} \mathbf{r}_{\alpha} \right),$$

where Z_{α} is the nuclear charge number of the α nuclei.

In order to derive the working Hamiltonian for the rovibrational motion in an electric field, this Hamiltonian is first transformed to the center of mass frame and then to a rotating molecule fixed frame with the origin at the center of mass of the nuclei, which introduces the total orbital angular momentum. Using the Born-Oppenheimer approximation the nuclear equation of motion in the presence of the field is derived, where several coupling terms, such as Coriolis couplings, appear. Due to the ${}^1\Sigma^+$ symmetry of the electronic ground state some of those coupling terms vanish. From the remaining ones we extract those that are relevant for an accurate description of the rovibrational motion in the presence of the field. We consider here the regime where perturbation theory holds for the description of the electronic structure but a nonperturbative treatment is indispensable for the corresponding nuclear dynamics. The resulting Hamiltonian for the rovibrational motion reads

$$\mathcal{H} = -\frac{\hbar^2}{2R^2\mu} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{\mathbf{J}^2(\theta, \phi)}{2\mu R^2} + \varepsilon(R) - F(\cos \theta)D(R), \quad (1)$$

where R and θ, ϕ are the internuclear coordinate and Euler angles, respectively. μ is the reduced mass of the nuclei, $\mathbf{J}(\theta, \phi)$ the orbital angular momentum, $\varepsilon(R)$ represents the field-free electronic potential energy curve (PEC), and $D(R)$ the electronic dipole moment function (EDMF).

In the framework of the rigid rotator approach, the rovibrational Hamiltonian (1) reduces to

$$\mathcal{H} = \frac{\mathbf{J}^2}{2\mu R_{eq}^2} - F(\cos \theta)D_{eq}, \quad (2)$$

where R_{eq} and D_{eq} are the equilibrium internuclear distance and the corresponding dipole moment. For diatomic molecules, this rigid rotator Hamiltonian is integrable and it was solved numerically in Ref. [26]. Our approach goes beyond this rigid rotator description, taking into account the rotation-vibration coupling and the dependence of the dipole moment on the vibrational coordinate. It is to be expected that the latter are of particular importance for highly excited vibrational states.

In the field-free case each state is characterized by its vibrational ν , 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 nonintegrable two-dimensional Schrödinger equation in (R, θ) space. In order to solve the rovibrational equation of motion associated with the Hamiltonian (1), we developed a hybrid computational approach. The latter combines discrete and basis set methods, applied to the vibrational and rotational degrees of freedom, respectively. For the angular part a basis set expansion in terms of spherical harmonics is used, taking into account that M is conserved. The vibrational degree of freedom is treated by a discrete variable representation. Due to the typical shape of molecular PECs, we chose the radial harmonic oscillator discrete variable representation, where the odd harmonic oscillator functions are taken

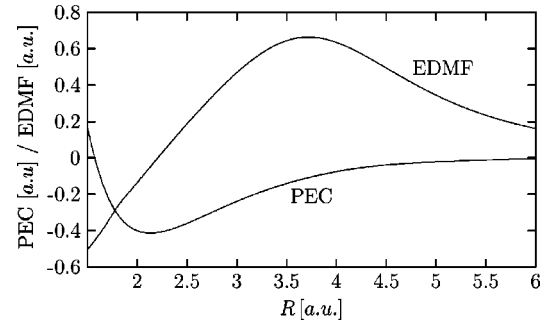


FIG. 1. Electronic potential energy curve and electric dipole moment function of the electronic ground state of carbon monoxide. Both quantities are given in atomic units.

as basis functions. 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.

III. POTENTIAL ENERGY CURVE AND ELECTRONIC DIPOLE MOMENT FUNCTION

The PEC represents the key to the rovibrational spectrum and the EDMF determines the strength of the interaction of the rovibrational states with the electric field. Due to the fact that we are interested in highly excited rovibrational states in an electric field we need the PEC and the EDMF not only in the neighborhood of the equilibrium internuclear distance, but for a very broad range of the internuclear distances covering the short, intermediate, and long range behavior.

Motivated by the special shape of the EDMF of carbon monoxide, we have chosen it as a prototype to present and discuss our results. 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} . The expectation value $\langle \psi_{\nu 0} | D(R) | \psi_{\nu 0} \rangle$, $\psi_{\nu 0}(R)$ being the field-free wave function of the ν th vibrational state with $J=0$, possesses a maximum for a certain highly excited vibrational state. Thus, the influence of the external field is significantly more pronounced for the high-lying excited states compared to the rovibrational ground state. The typical cases discussed in the literature address exclusively low-lying states localized in the intermediate neighborhood of R_{eq} .

To construct the EDMF for the above-indicated broad regime Padé approximation techniques [28] are employed, using experimental absolute and relative intensities and the appropriate numerically computed wave functions, possessing the correct asymptotic behavior. For other molecular systems one might have only some values of the EDMF around R_{eq} , and it will be necessary to extrapolate it to shorter and larger distances taking into account the correct asymptotic behavior.

For the electronic ground state of the CO molecule an accurate experimental potential [Rydberg-Klein-Rees (RKR)

[29]], generated by Spielfiedel and Tchang-Brillet [30], based on the high-precision measurements of Le Floch [31] is available. These data provide us with an excellent description of the potential well centered around R_{eq} . To extend it to larger distances, especially the asymptotic behavior, we have used an analytical expression for the long range behavior, and an empirical intermediate potential connecting the potential well with the asymptotic long range behavior [32]. The short range behavior is provided by a Morse potential fitted to the corresponding RKR data. The connection between the different regimes is done by means of a cubic interpolation, providing a smooth and very accurate PEC.

IV. RESULTS

Applying the method described in Sec. II to solve the rovibrational Schrödinger equation, we have performed extensive computations providing the eigenfunctions and spectrum. The expectation values $\langle \cos \theta \rangle$ and $\langle J^2 \rangle$ and the dipole strengths of corresponding rovibrational transitions have been computed. Our focus is the regime $F=0.0-10^{-4}$ a.u., i.e., $F=(0.0-5.14)\times 10^7$ V/m (1 a.u. of field strength corresponds to 5.14×10^{11} V/m), covering the experimentally available static field strengths. In view of the large number of vibrationally bound states with $J=0$ of the CO molecule in field-free space, which is more than 80, we will focus on the states evolving from the field-free states for small values of the angular momentum J and $M=0$. In the following we will frequently refer to the vibrational and rotational quantum numbers ν and J of the states without field even in the presence of the field. Although this procedure facilitates the description of our results, it should not obscure the fact that the only good quantum number in the presence of the field is the magnetic quantum number M . Mixing of states with different vibrational quantum numbers ν becomes relevant only for very highly excited states and for very strong fields.

We would like to point out the high accuracy and efficiency of our numerical approach: we can trace in the presence of the field almost all vibrational bound states for $F=0$, thereby providing accurate data on 77 vibrational states evolving from either $J=0$ or $J=1$ for $F=0$. The energy spacing and the expectation values are obtained with a typical relative accuracy of 10^{-6} . Atomic units will be used throughout unless stated otherwise.

A. Rovibrational spectra

In order to analyze the effect of the electric field on the rovibrational spectra, we introduce the following parameter:

$$\kappa = \frac{E_{\nu 0}(0) - E_{\nu 0}(F)}{E_{\nu 1}(F) - E_{\nu 0}(F)}, \quad (3)$$

where $E_{\nu 0}(F)$ and $E_{\nu 1}(F)$ are the ν th vibrational states with $J=0$ and $J=1$, respectively, for the field strength F . It is the ratio of the energy shift of the state $(\nu, 0)$, due to the field, compared to the energy level spacing in the presence of the field. The larger κ is, the larger is the influence of the field on the spectrum. In particular, for κ of the order of magnitude

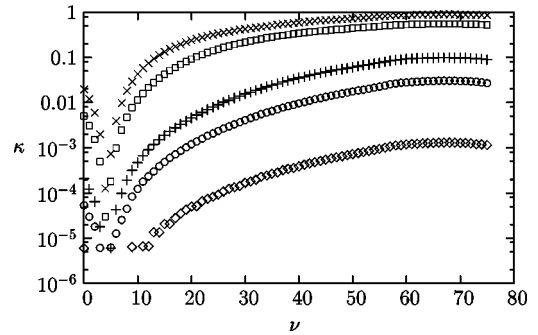


FIG. 2. The parameter κ (see text) as a function of the vibrational number ν of states with $J=0$ in the absence of the field, for several field strengths $F=10^{-6}$ (\diamond), 5×10^{-6} (\circ), 10^{-5} ($+$), 5×10^{-5} (\square), and 10^{-4} (\times) a.u.

of 1 the spectrum in the presence of the field and without field have almost nothing in common. Figure 2 illustrates the behavior of κ as a function of ν for each state, and compares it for several field strengths $F=10^{-6}$, 5×10^{-6} , 10^{-5} , 5×10^{-5} , and 10^{-4} a.u.

For the complete spectra we encounter $\kappa > 0$, i.e., in the presence of the electric field the states become more bound than without field. This trend continues steadily as the field strength is increased. The values of κ obtained for states with $\nu=2-8, 10$ and $F=10^{-6}$ a.u. are too small to be included in Fig. 2. For all field strengths κ shows a similar behavior as a function of the degree of excitation ν . Starting with $\nu=0$ κ first decreases and possesses a minimum for the state with $\nu=4$. Thereafter it increases monotonically with increasing ν up to very high excitations. For $\nu=68$ a maximum is reached, and a decay of κ follows on further increasing ν . $\kappa(\nu)$ shows a very weak dependence on ν around its maximum. For a fixed field strength κ varies by several orders of magnitude (up to four) when moving through the spectrum, indicating a dramatic change of the response of the molecule to the field. Let us illustrate this for $F=10^{-4}$ a.u.: for the rovibrational ground state $\nu=0$, we have $\kappa=1.95\times 10^{-2}$, for the state with $\nu=4$, $\kappa=1.24\times 10^{-4}$, for the state with $\nu=40$, $\kappa=0.592$, and at the maximum $\nu=68$, $\kappa=0.896$. For the low-lying states, an increase with respect to the field strength of one order of magnitude produces a change of κ of approximately two orders of magnitude. This factor decreases for higher excitations. For levels with $\nu\sim 70$, an enhancement of one order of magnitude with respect to the field strength leads to an increase of κ by one order of magnitude. Although an increase of the field strength produces a larger relative change of κ for the low-lying states, its absolute change is comparatively small in this regime, and the effects due to the field are most pronounced for energetically highly excited states. The latter is also natural because the EDMF has its maximum at large internuclear distances which are probed significantly only by higher excited states.

B. Expectation values: $\langle J^2 \rangle$, $\langle \cos \theta \rangle$, and $\Delta \cos \theta$

Figure 3 shows the expectation value $\langle J^2 \rangle$ of states possessing a spherical symmetry for $F=0$ as a function of the vibrational label ν for the field strengths $F=5$

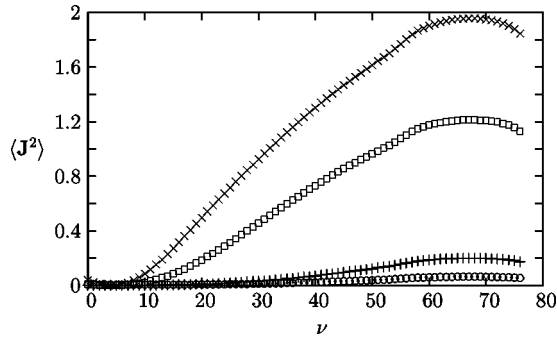


FIG. 3. The expectation value $\langle J^2 \rangle$, as a function of the vibrational number ν of states with $J=0$ in the absence of the field, for several field strengths $F=5 \times 10^{-6}$ (\circ), 10^{-5} ($+$), 5×10^{-5} (\square), and 10^{-4} (\times) a.u.

$\times 10^{-6}$, 10^{-5} , 5×10^{-5} , and 10^{-4} a.u. $\langle J^2 \rangle$ provides a measure for the mixture of states for $F=0$ with different rotational quantum numbers J but the same value for M , i.e., it describes 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, as already indicated when studying the corresponding behavior of $\kappa(\nu)$. For all field strengths $\langle J^2 \rangle$ shows qualitatively a similar but quantitatively very different behavior as a function of ν . $\langle J^2 \rangle$ passes through a minimum for the state with $\nu=4$, where the influence of the external field is almost negligible. Generally, for $\nu \leq 10$ the mixture of $F=0$ rotational states is very minor for all field strengths considered here. With further increasing ν the mixing of states becomes more pronounced and $\langle J^2 \rangle$ monotonically increases up to the maximum for $\nu=68$. The range of J values contributing to each state becomes significantly larger as the field strength increases. The behavior of $\langle J^2 \rangle$ with the vibrational quantum number ν can be explained by means of the field-free expectation value of the EDMF; $\langle \psi_{\nu 0} | D(R) | \psi_{\nu 0} \rangle$ increases as ν increases, reaching its minimum absolute value for $\nu=4$ and its maximum for $\nu=54$. This point will be addressed again in Sec. VI. In order to illustrate the differences of low-lying compared to highly excited states, we present in Table I the value of $\langle J^2 \rangle$ for the rovibrational ground state and for the level for which $\langle J^2 \rangle$ possesses its maximum. The corresponding energies in the absence of the field are $E_0 = -0.408212$ a.u. and $E_{68} = -0.010334$ a.u. A comparison shows that $\langle J^2 \rangle$ is much larger for the highly excited state than for the rovibrational ground state.

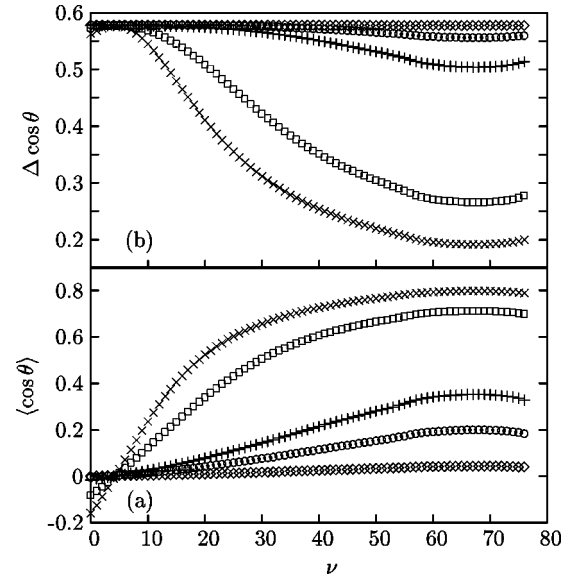


FIG. 4. The expectation values $\langle \cos \theta \rangle$ (a) and $\Delta \cos \theta$ (b) as a function of the vibrational number ν of states with $J=0$ in the absence of the field, for the same field strengths as in Fig. 2.

Figure 4(a) illustrates the behavior of the expectation value $\langle \cos \theta \rangle$ as a function of the degree of excitation ν for the same values of the field as in Fig. 2. The corresponding results for $\Delta \cos \theta = \sqrt{\langle \cos^2 \theta \rangle - \langle \cos \theta \rangle^2}$ are included in Fig. 4(b). The closer $\Delta \cos \theta$ is to zero, the stronger is the alignment of the state, and the closer the absolute value of $\langle \cos \theta \rangle$ is to 1, the stronger is the orientation of the state along the field. Of course any small value for $\Delta \cos \theta$ together with a certain value for $\langle \cos \theta \rangle$ would indicate a preferred direction of the molecular axis. Let us momentarily focus on the behavior of $\langle \cos \theta \rangle$ [Fig. 4(a)]. Due to the spherical symmetry of the states at $F=0$, we have $\langle \cos \theta \rangle = 0$. For $F \neq 0$ a mixture of different states occurs and thus in general $\langle \cos \theta \rangle \neq 0$. For all field strengths considered, $\langle \cos \theta \rangle$ monotonically increases with increasing degree of excitation. $\langle \cos \theta \rangle$ is maximal for the state $\nu=68$ and decreases thereafter. Only for the states $\nu \leq 4$ is $\langle \cos \theta \rangle$ negative. This change of sign reflects the change of the sign that the EDMF of the CO molecule exhibits for $R > R_{eq}$, indicating that the states with $\nu \leq 4$ are oriented in the opposite direction to the field, while the states with $\nu > 4$ are in the field direction. For a certain state the orientation increases with increasing field strength. The absolute changes are largest for highly excited states. For $F=10^{-4}$ a.u., e.g., states with a field-free energy $E >$

TABLE I. Expectation values $\langle J^2 \rangle$ and $\langle \cos \theta \rangle$ for the rovibrational ground state and a highly excited state $\nu=68$, $J=0$, for several field strengths.

F	$\langle J^2 \rangle_0$	$\langle \cos \theta \rangle_0$	$\langle J^2 \rangle_{68}$	$\langle \cos \theta \rangle_{68}$
10^{-6}	4.07×10^{-6}	-1.64×10^{-3}	2.521×10^{-3}	4.098×10^{-2}
5×10^{-6}	1.017×10^{-4}	-8.175×10^{-3}	5.915×10^{-2}	0.1964
10^{-5}	4.068×10^{-4}	-1.647×10^{-2}	0.2002	0.3519
5×10^{-5}	1.006×10^{-2}	-8.175×10^{-2}	1.2135	0.7122
10^{-4}	3.897×10^{-2}	-0.1600	1.9570	0.7977

-0.06 a.u., i.e., $\nu > 50$, already show a significant orientation $0 < \theta \leq 40^\circ$. 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. See Table I for a numerical comparison of the values of $\langle \cos \theta \rangle$ for the states $\nu=0$ and $\nu=68$. $\Delta \cos \theta$ in Fig. 4(b) clearly indicates that the spreading of the field-hybridized angular motion decreases strongly with increasing field strength F and degree of excitation ν .

C. Rovibrational spectral transitions

For heteronuclear diatomic molecules, rovibrational electric dipole transitions within the same electronic state are possible. In the presence of a strong external field only the selection rule $\Delta M = 0, \pm 1$ remains. We focus on the rovibrational transitions with $\Delta M = 0$ and on two kinds of rotational spectral transitions (see below). The transitions are characterized by their dipole strengths (DSs)

$$d_{\alpha\beta} = |\langle \psi_\alpha | D(R) \cos \theta | \psi_\beta \rangle|^2, \quad (4)$$

where ψ_α and ψ_β are the wave functions of the initial and final (eigen)states, respectively.

Let us start by addressing the results on the rovibrational transitions between the states $(\nu, 0) \rightarrow (\nu', 1)$ with $\Delta \nu = \nu' - \nu = 0, 1, 2$, which are allowed transitions for $F=0$. Figures 5(a), 5(b), and 5(c) present the DS as a function of the vibrational number ν of the initial state for the transitions with $\Delta \nu = 0, 1$, and 2 , respectively, and $F = 0, 10^{-5}, 5 \times 10^{-5}$, and 10^{-4} a.u. Field strengths below $F = 5 \times 10^{-6}$ a.u. cause only tiny changes of the DS and are therefore not included in Fig. 5. We begin with an analysis of the transitions $\Delta \nu = 0$ and $F = 0$. For energetically low-lying states, the DS decreases as ν increases. There appears to be a very pronounced minimum for the state $\nu = 4$. Beyond this point, the DS monotonically increases with increasing ν by several orders of magnitude and passes through a maximum for the transition with $\nu = 54$ for $F = 0$, and then monotonically decreases thereafter. In the neighborhood of the maximum a plateaulike behavior is observed. The behavior of the DS is qualitatively similar for all nonzero field strengths. The main differences are that the position of the maximum is shifted to lower values of ν for increasing F and the plateaulike structure becomes more pronounced. For $F = 10^{-4}$ a.u. the maximum is reached for the states with $\nu = 45$. An increase of the field strength generally causes a decrease of the corresponding DS: for small values of ν this effect is much less pronounced than for large values. Indeed, the effects of a finite field on the DS for $\nu \leq 10$ are hardly visible in Fig. 5(a). Equally, the DSs for $F = 0$ and $F = 10^{-5}$ a.u. are practically the same on the scale given in Fig. 5(a) except for transitions with $\nu > 50$ where a minor change is observed. For $F = 5 \times 10^{-5}$ a.u. and $F = 10^{-4}$ a.u. transitions involving $\nu \geq 15$ show strong deviations from the corresponding field-free values. The absolute values of the DS for $F = 10^{-4}$ a.u. compared to $F = 0$ for $\nu \geq 50$ are different by approximately one order of magnitude.

Similar conclusions are obtained for the transitions $\Delta \nu$

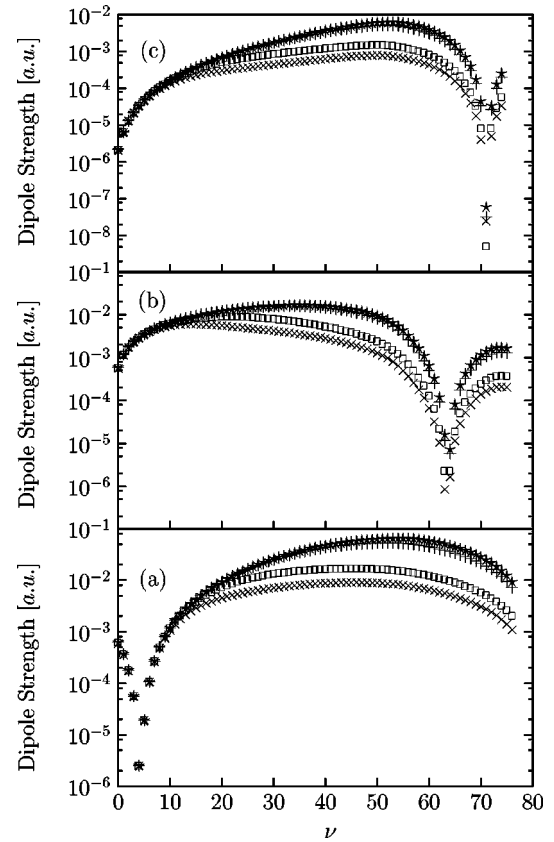


FIG. 5. Dipole strengths of the transitions $(\nu, 0) \rightarrow (\nu, 1)$ (a), $(\nu, 0) \rightarrow (\nu + 1, 1)$ (b), and $(\nu, 0) \rightarrow (\nu + 2, 1)$ (c) as a function of the vibrational number of the initial states, for the field strengths $F = 0.0$ (\star), 10^{-5} ($+$), 5×10^{-5} (\square), and 10^{-4} (\times) a.u.

$= 1$ and 2 [see Figs. 5(b) and 5(c), respectively], possessing overall smaller DSs than the transitions $\Delta \nu = 0$. The main difference with respect to the $\Delta \nu = 0$ case is the absence of a sharp minimum for $\nu = 4$. Instead, such a feature occurs for large values of ν . For $\Delta \nu = 1$, this minimum appears for $F = 0$ and $F = 10^{-5}$ a.u. for the transition emanating from $\nu = 64$, for $F = 5 \times 10^{-5}$ a.u. and $F = 10^{-4}$ a.u. we have $\nu = 63$. For $\Delta \nu = 2$, this minimum appears for all field strengths for the transitions with the initial state $\nu = 72$. The field-free positions of the minima can be explained in terms of the expectation values $|\langle \psi_{\nu 0} | D(R) | \psi_{\nu+1 1} \rangle|$ and $|\langle \psi_{\nu 0} | D(R) | \psi_{\nu+2 1} \rangle|$, which acquire their smallest values for the corresponding ν . Again, an increase of the electric field strength causes a decrease of the DS.

One of the main effects of the electric field on the rovibrational spectra is the large number of allowed transitions that are forbidden without field. We illustrate it with the DSs for the rovibrational transitions $(\nu, 0) \rightarrow (\nu', 0)$ with $\Delta \nu = 1, 2, 3$ in Figs. 6(a), 6(b), and 6(c), respectively. Let us first focus on the transitions $\Delta \nu = 1$, in Fig. 6(a). Now an increase of F produces an increase of the DS which, depending on ν , is more or less pronounced. The DS behaves qualitatively similarly for all values of F considered. It possesses two sharp minima, for small and large values of ν and in between a very smooth, approximately linear behavior reaching a maximum, that shifts to lower values of ν with increasing F .

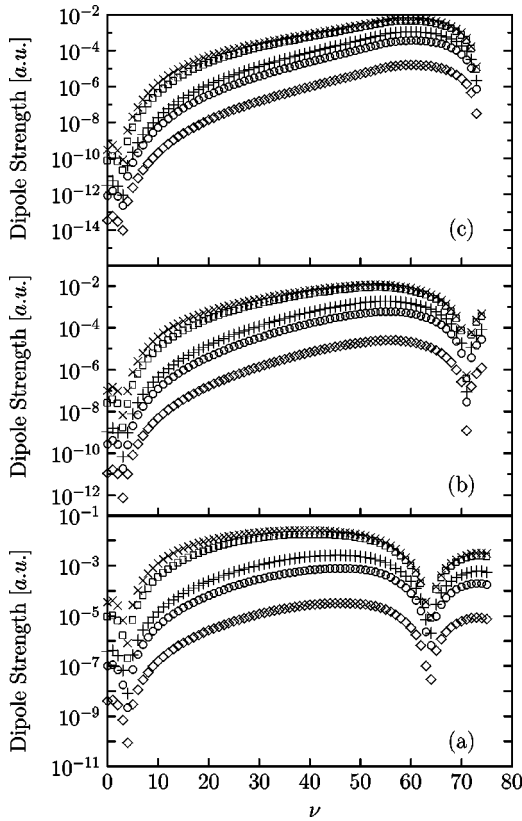


FIG. 6. Dipole strength of the transitions $(\nu,0) \rightarrow (\nu+1,0)$ (a), $(\nu,0) \rightarrow (\nu+2,0)$ (b), and $(\nu,0) \rightarrow (\nu+3,0)$ (c), as a function of the vibrational number of the initial states, for the same field strengths as in Fig. 2.

The first minimum appears always for the transition involving the state $\nu=4$ and the second one is at $\nu=62$ for $F=10^{-6}$ a.u. and for all other field strengths at $\nu=64$. The maximum is shifted from $\nu=46$ for the lowest field strength to $\nu=39$ for the highest. For a certain transition the increase of the field strength from $F=10^{-6}$ a.u. to 5×10^{-6} a.u. causes an increase of one order of magnitude or even more for the DS. Enhancing the field from $F=5 \times 10^{-6}$ a.u. to $F=10^{-5}$ a.u. a correspondingly smaller increase is observed. Due to the minor hybridization of the rotational motion for $\nu \lesssim 10$, their DSs are very small. The results obtained for the transitions $\Delta\nu=2$ and 3 [see Figs. 6(b) and 6(c), respectively] show similar properties as for $\Delta\nu=1$. Of course, an increase of $\Delta\nu$ produces a general decrease of the DS, i.e., the weighted overlap between non-neighboring vibrational states decreases.

V. ADIABATIC SEPARATION OF ANGULAR AND RADIAL MOTION IN THE PRESENCE OF THE FIELD

In this section we develop an approach to solve the rovibrational Schrödinger equation belonging to the Hamiltonian (1) by performing an adiabatic separation of the (R, θ) motion, i.e., the radial and angular motions as we shall call them in the following. We thereby derive an “effective rotor Hamiltonian” describing the angular motion of the molecule in an electric field. The corresponding effective equation of

motion describes to a very good accuracy the effect of the electric field on the rovibrational motion of the molecular systems.

Let P_R , P_θ , and P_ϕ be the conjugate momenta of the nuclei belonging to the vibrational coordinate R and Euler angles (θ, ϕ) . The Hamiltonian (1) describing the rovibrational motion in an electric field is written as follows in term of the canonical pairs:

$$\mathcal{H} = \frac{1}{2\mu} \left[P_R^2 + \frac{1}{R^2} P_\theta^2 + \frac{1}{R^2 \sin^2 \theta} P_\phi^2 \right] + \epsilon(R) - FD(R) \cos \theta. \quad (5)$$

It is clear from this expression that ϕ is a constant of motion, and one can separate ϕ by using as wave function $\Psi(R, \theta, \phi) = \Psi_M(R, \theta) e^{iM\phi}$, with M the magnetic quantum number of the state. For simplicity we restrict our analysis to $M=0$ states. The validity of the following discussion is restricted to those molecular systems and states for which the energy scales associated with the rotational and vibrational motions differ by several orders of magnitude.

Let us assume that the vibrational problem has been solved for a specific value of the rotational coordinate θ , assuming $P_\theta \rightarrow 0$,

$$\left[\frac{1}{2\mu} P_R^2 + \epsilon(R) - FD(R) \cos \theta \right] \psi_\nu(R; \theta) = E_\nu(\theta) \psi_\nu(R; \theta), \quad (6)$$

where $\psi_\nu(R; \theta)$ is a member of the orthonormal vibrational wave functions labeled by ν . $\psi_\nu(R; \theta)$ depends parametrically on the angle θ . Making the following ansatz for the rovibrational wave function:

$$\Psi_0(R, \theta) = \sum_\nu \psi_\nu(R; \theta) \chi_\nu(\theta),$$

and inserting it in the rovibrational equation of motion belonging to the Hamiltonian (1), after left multiplication with $\psi_\nu^*(R; \theta)$ and performing the integral over R , using the orthonormality of the vibrational functions as well as Eq. (6) and keeping in mind that \mathbf{J}^2 is an operator,

$$\left[\frac{1}{2\mu} \langle R^{-2} \rangle_\nu \mathbf{J}^2 + E_\nu(\theta) - E \right] \chi_\nu(\theta) + \sum_\kappa \left(\frac{A_{\nu\kappa}^2}{2} + A_{\nu\kappa}^1 \mathbf{J} \right) \chi_\kappa(\theta) + \sum_{\kappa \neq \nu} \frac{A_{\nu\kappa}^0}{2} \mathbf{J}^2 \chi_\kappa(\theta) = 0 \quad (7)$$

with

$$\langle R^{-2} \rangle_\nu = \int_0^\infty \psi_\nu^*(R; \theta) \psi_\nu(R; \theta) dR,$$

$$A_{\nu\kappa}^i = \frac{1}{\mu} \int_0^\infty \psi_\nu^*(R; \theta) \mathbf{J}^i \psi_\kappa(R; \theta) dR, \quad i=0,1,2. \quad (8)$$

If these coupling coefficients were all equal to zero, Eq. (7) would reduce to a single channel equation and an adiabatic

separation of the angular and radial motion would have been achieved. $E_\nu(\theta)$ serves then as a potential for the motion in θ space.

Let us briefly discuss the case $F=0$. In this case the separation of the radial and angular motions is exact in the sense that the exact rovibrational eigenfunction is a product of a vibrational $\psi_{\nu,J}(R)$ and a rotational $Y_{JM}(\theta, \phi)$ part. In the above adiabatic separation the J dependence of the vibrational motion is neglected [see Eq. (6)], the centrifugal term scales as proportional to $1/\mu$, and is dominated by the PEC $\epsilon(R)$ for small values of J . Different rotational excitations possess within this approximation the same vibrational wave function $\psi_{\nu,0}(R)$. For $F=0$, the coefficients $A^2=A^1=0$ and A^0 provides a residual coupling.

We can then introduce a further approximation, assuming that (for certain molecules) the influence of the electric field on the vibrational motion is very small and can therefore be described by perturbation theory. This concept is meaningful if the energy scales associated with the rotational and vibrational motions are well separated. Then, one expands the vibrational wave functions and energies according to

$$\psi_\nu(R; \theta) \approx \psi_\nu^{(0)}(R) + \psi_\nu^{(1)}(R; \theta),$$

$$E_\nu(\theta) \approx E_\nu^{(0)} + E_\nu^{(1)}(\theta),$$

where $\psi_\nu^{(0)}(R) = \psi_{\nu,0}(R)$ and $E_\nu^{(0)} = E_{\nu,0}$ are the field-free quantities and only first order corrections have been included. We have

$$E_\nu^{(1)}(\theta) = -F \cos \theta \langle D(R) \rangle_\nu^{(0)}$$

$$\text{with } \langle D(R) \rangle_\nu^{(0)} = \langle \psi_\nu^{(0)} | D(R) | \psi_\nu^{(0)} \rangle.$$

Using these expressions in the rotational equation (7), evaluating the coupling coefficients (8), neglecting all terms of higher order in the wave function $\psi_\nu(R; \theta)$, and assuming that the coupling between different vibrational states is very small, one arrives at

$$\begin{aligned} \mathcal{H}_\nu^{\mathcal{R}} \chi_\nu(\theta) = \chi_\nu(\theta) E \quad \text{with} \quad \mathcal{H}_\nu^{\mathcal{R}} = \frac{1}{2\mu} \langle R^{-2} \rangle_\nu^{(0)} \mathbf{J}^2 \\ - F \cos \theta \langle D(R) \rangle_\nu^{(0)} + E_\nu^{(0)} \end{aligned} \quad (9)$$

with $\langle R^{-2} \rangle_\nu^{(0)} = \langle \psi_\nu^{(0)} | R^{-2} | \psi_\nu^{(0)} \rangle$. In this way, we have obtained an effective rotational equation of motion, providing us with an ‘‘effective rotor Hamiltonian’’ $\mathcal{H}_\nu^{\mathcal{R}}$, defined for each vibrational state ν . In $\mathcal{H}_\nu^{\mathcal{R}}$ 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 $\langle D(R) \rangle_\nu^{(0)}$, and the last one is just a shift of the energy. Our effective rotor Hamiltonian (9) looks different for each vibrational state since it explicitly contains the expectation values $\langle R^{-2} \rangle_\nu^{(0)}$ and $\langle D(R) \rangle_\nu^{(0)}$. Therefore $\mathcal{H}_\nu^{\mathcal{R}}$ describes an effective vibrational state-dependent angular motion. A similar procedure to the above one has been pursued to describe nuclear collective rotations in Ref. [33].

Let us comment on how to solve the resulting equations (6) and (9) of the above scheme. In a first step, the vibrational equation (6) for $F=0$ is integrated by means of the discrete variable approach, obtaining the vibrational spectrum $E_\nu^{(0)}$ and the corresponding expectation values $\langle R^{-2} \rangle_\nu^{(0)}$ and $\langle D(R) \rangle_\nu^{(0)}$. After introducing these quantities in the effective rotational equation of motion (9), it is solved by means of a basis set expansion with respect to the associated Legendre polynomials.

The main difference of the effective rotor Hamiltonian (9) compared to the traditional rigid rotator Hamiltonian (2) is that the expression (9) involves specific characteristics of each vibrational state via the expectation values $\langle R^{-2} \rangle_\nu^{(0)}$ and $\langle D(R) \rangle_\nu^{(0)}$. This is why $\mathcal{H}_\nu^{\mathcal{R}}$ is capable of describing highly excited rovibrational states exposed to the external field whereas Eq. (2) cannot do so. To see this explicitly it is instructive to compare R_{eq}^{-2} with $\langle R^{-2} \rangle_\nu^{(0)}$: with increasing ν they show significant deviations.

VI. COMPARISON OF THE FULL ROVIBRATIONAL COMPUTATION WITH THE ADIABATIC SEPARATION

In this section we compare our results obtained by solving the Schrödinger equation belonging to the Hamiltonian (1) with those following the above adiabatic scheme. As was already emphasized, the validity of this approach is restricted to those molecular systems and states for which the coupling between the rotational and vibrational motions is very small. We define the following relative difference between the results obtained in both approaches:

$$\Delta A_\nu = \frac{|A_\nu^{\mathcal{F}} - A_\nu^{\mathcal{R}}|}{A_\nu^{\mathcal{F}}},$$

where $A_\nu^{\mathcal{F}(\mathcal{R})}$ represents one of the quantities $\Delta E_\nu^{\mathcal{F}(\mathcal{R})}$, $\langle \cos \theta \rangle_\nu^{\mathcal{F}(\mathcal{R})}$, $\langle \cos^2 \theta \rangle_\nu^{\mathcal{F}(\mathcal{R})}$, or $\langle J^2 \rangle_\nu^{\mathcal{F}(\mathcal{R})}$, \mathcal{F} indicates that they have been computed in the framework of the full rovibrational description and \mathcal{R} refers to the effective rotor approach. The energy level spacing is defined as $\Delta E_\nu^{\mathcal{F}(\mathcal{R})} = E_{\nu+1}^{\mathcal{F}(\mathcal{R})} - E_{\nu,0}^{\mathcal{F}(\mathcal{R})}$. Here, we present only the results of the analysis done for the strongest field $F=10^{-4}$ a.u. The comparisons for lower field strengths show similar results. Figure 7 illustrates the relative difference for the energy spacing as a function of ν . The corresponding results for the given three expectation values above are shown in Fig. 8. For the energy level spacings the agreement between both schemes is excellent. For the state with $\nu=65$ we obtain the highest relative difference $\Delta[\Delta E_{65}] \approx 3.2 \times 10^{-3}$. A similar conclusion holds for the comparison of the expectation values. For the $\nu=4$ state $\Delta \langle \cos \theta \rangle_4 \approx 1.6 \times 10^{-3}$ and $\Delta \langle J^2 \rangle_4 \approx 3.5 \times 10^{-3}$ are the highest relative differences for both quantities. Except for the $\nu=5$ state with $\Delta \langle J^2 \rangle_5 \approx 2.5 \times 10^{-3}$, the rest of the states of the spectra satisfy $\Delta \langle J^2 \rangle_\nu < 10^{-3}$ and $\Delta \langle \cos \theta \rangle_\nu < 10^{-3}$. Further, we obtain $\Delta \langle \cos^2 \theta \rangle_\nu < 10^{-4}$ for all the states. From these results one concludes that the effective rotor approach provides an excellent description of the influence of an electric field on the rovibrational spectrum of the CO molecule

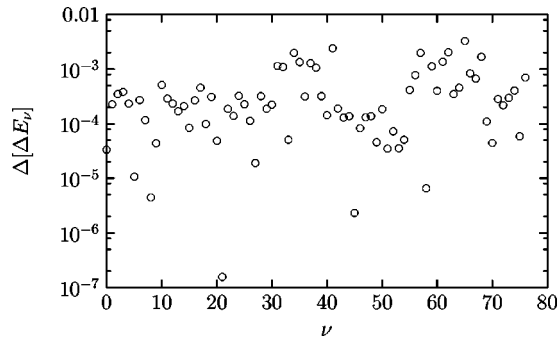


FIG. 7. Relative difference between the energy level spacing obtained with the full rovibrational description and by means of the effective rotor Hamiltonian, as a function of the vibrational number for $F = 10^{-4}$ a.u.

for the considered states. This is by no means restricted to the CO molecule but expected to hold for a broad variety of molecular species.

The expression of the effective rotor Hamiltonian (9) allows us to define a new effective rotor parameter

$$\omega_\nu = \frac{\langle D(R) \rangle_\nu^{(0)}}{\langle R^{-2} \rangle_\nu^{(0)}}$$

for each vibrational state ν , which specifies how strong is the interaction of its associated rotational band with an electric field. For the field-free vibrational spectra of the CO molecule this parameter monotonically increases as ν is increased, reaching a maximum for $\nu=68$, and decreasing thereafter monotonically. Moreover, we have $\omega_\nu > 0$ for $\nu > 4$ and $\omega_\nu < 0$ for $0 \leq \nu \leq 4$, making clear why the last group of states are oriented in the opposite direction compared to the complementary part of the spectrum. This parameter has the lowest absolute value for $\nu=4$, $\omega_4 = -0.0131$ and the highest one for $\nu=68$, $\omega_{68} = 4.927$, explaining why the effect of the field on these states were the least and most pronounced, respectively. In particular, it explains why $\langle \mathbf{J}^2 \rangle$ reaches its maximum value for the state with $\nu=68$. The large difference between the ω_ν values of these two levels (two orders of magnitude) illustrates that, depend-

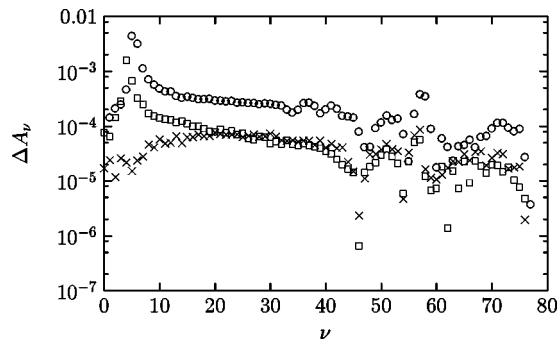


FIG. 8. Relative difference between the expectation value $\langle J^2 \rangle$ (○) computed with the full rovibrational description and by means of the effective rotor Hamiltonian, as a function of the vibrational number for $F = 10^{-4}$ a.u. Similar results for $\langle \cos \theta \rangle$ (□) and $\langle \cos^2 \theta \rangle$ (×) are also presented.

ing on the part of the rovibrational spectrum under consideration, a broad variety of responses to the electric field might be expected for the same molecule. For these so called “non-flexible” diatomic molecules the PEC and EDMF play a key role in order to determine which part of the rovibrational spectra will be affected by the external field in a significant way. This could be exploited in the framework of state-to-state chemical reaction dynamics, and also in cold molecular physics via the preparation of the molecule in a highly oriented and hybridized rovibrational state.

Within the present adiabatic approximation we assign to each rotational band a single vibrational wave function, i.e., $\psi_{\nu 0}(R)$. Beyond this approximation it is possible to consider for each rovibrational state a different vibrational wave function, e.g., its field-free wave function $\psi_{\nu J}(R)$, which takes into account the field-free rotational quantum number of the state. We have seen that the improvement for the description of the above discussed quantities will be very small, since the agreement of the exact and effective rotor results is excellent. However, for a proper description of the rovibrational transitions the latter improvement plays an important role due to the difference between the expectation values $\langle \psi_{\nu 0} | D(R) | \psi_{\nu 1} \rangle$ and $\langle \psi_{\nu 0} | D(R) | \psi_{\nu 0} \rangle$, which appear in the computation of the dipole strengths.

VII. CONCLUSIONS AND OUTLOOK

We have investigated the rovibrational structure of carbon monoxide in an electric field, serving as a prototype heteronuclear diatomic molecule. Our approach was as comprehensive as currently possible by treating the fully coupled rovibrational motion and taking into account the dependence of the electric dipole moment on the internuclear distance. We hereby assumed that the external electric field affects the rovibrational dynamics in a nonperturbative way, whereas the influence on the electronic structure can be described by means of perturbation theory. The Schrödinger equation for the rovibrational motion was solved by a highly efficient and accurate (nonperturbative) computational approach being a combination of a discrete variable representation method and a basis set expansion, applied to the vibrational and rotational coordinates, respectively. We would like to remark that, although the accuracy and efficiency of this computational scheme is demonstrated here for the CO molecule it should be equally applicable to any other heteronuclear diatomics possessing a $^1\Sigma^+$ electronic ground state.

Due to the many field-free rovibrational bound states of the CO molecule we have focused on the study of states that belong to small values of the rotational quantum number J and have $M=0$ in the field-free case. Depending on the state under consideration and on the field strength the influence of the electric field on relevant quantities such as the energy varies by several orders of magnitude. It is an overall tendency that the states become stronger bound with increasing field strength. The orientation, hybridization, and mixing of field-free rotational states were illustrated with the help of several expectation values for $F = 10^{-6} - 10^{-4}$ a.u., $F = 5.14 \times 10^5 - 5.14 \times 10^7$ V/m, being within the regime of experimental interest. In particular, we have shown how the

range of J values contributing to a certain state increases with increasing field strength, this effect being very pronounced for high-lying states, e.g., for $\nu=68$ and $F=10^{-4}$ a.u. we obtained $\langle \mathbf{J}^2 \rangle = 1.957$. While for all considered field strengths low-lying states present a very small degree of orientation, for highly excited states and $F=10^{-4}$ a.u. a strong orientation is achieved, e.g., for $\nu=68$ we had $\langle \cos \theta \rangle = 0.7977$ and in general for $\nu > 50$ and the same field strength we obtained $0 < \theta \leq 40^\circ$. We have considered two kinds of rovibrational spectral transitions; the first group are allowed in the absence of the electric field, whereas the second group are allowed only due to the presence of the electric field. The evolution of their dipole strengths with increasing field strength is discussed. Our results illustrate how the $\Delta J=0$ transitions become allowed under an electric field and their dipole strengths increase with increasing field strength, whereas the dipole strengths of the $\Delta J=1$ transitions decrease.

An effective rotor Hamiltonian is derived that describes the influence of the external field on the spectra of a molecule, with a small coupling between the angular and radial motions. It is superior to the traditional rigid rotator Hamiltonian used frequently in the literature. Its major advantage is the introduction of the properties of each vibrational state, i.e., for each vibrational state there is a different effective rotor Hamiltonian individually accounting for its essential properties. The validity of this approach was demonstrated for the CO molecule by comparing with the results obtained from the solution of the fully coupled rovibrational Schrödinger equation. This allowed us to predict and explain the influence of the external field and to find out those rovibrational states that are going to be most affected by the field. It turns out that for CO these are vibrationally very highly excited states.

The vibrational state dependence of the effective rotor equation opens perspectives for the application of the external field to hybridize the rotational motion. Depending on the individual expectation values $\langle D(R) \rangle_\nu^{(0)}$ and $\langle R^{-2} \rangle_\nu^{(0)}$ for the many vibrational states of a certain molecule and depending on the heteronuclear species itself possessing different $D(R)$, a broad variety of possibilities of the hybridization, alignment, and orientation can easily be imagined. Molecules considered up to now as being inappropriate for achieving alignment or orientation, or a strong influence of the electric field on its properties in general, will have to be reconsidered as possible candidates, taking advantage of the variety of rovibrational states that potentially strongly interact with the electric field. In particular, it is considered to be experimentally very difficult to achieve any significant influence of a laboratory static electric field on the rovibrational low-lying states of the CO molecule [34]. This does not hold for its

high-lying rovibrational excited states, as shown in the present work.

From an experimental point of view one can think of several potential applications of our results. Depending on the EDMF $D(R)$ of a particular molecular species and its field-free vibrational wave functions one can expect and design a large variety of electric-field-dressed properties with changing electric field and in particular increasing degree of rovibrational excitation of the species. Moreover, going to electronically excited states still enriches these possibilities of obtaining new “patterns” of field-dressed properties throughout the rovibrational spectra. Obviously, one can then think of the selective control of chemical reaction dynamics: certain excited states, for example, are strongly hybridized by the electric field and show a different reaction dynamics compared to the nonhybridized ones. An adequate preparation of the initial rovibrational states of the reactants and the corresponding modification with an electric field will provide the proper initial conditions in order to optimize and control a chemical reaction. Influencing scattering inelastic cross sections or the control of dissociation dynamics could be possible.

In the present work we have been focusing on low-lying angular excitations. It is a natural next step to investigate the influence of the electric field on states that possess higher J values in the field-free case. Obviously, the rotation-vibration coupling will become increasingly more important and might invalidate the above developed state-dependent effective rotor approach for highly excited rotational states. Even more important and interesting is the perspective of investigating flexible molecules that possess a significant rotation-vibration mixing in the absence of the field. Nothing is known so far about the impact of the external electric field on the rovibrational motion and properties of these systems. Typical examples for the latter are the heteronuclear alkali-metal dimers, which are of major current interest with respect to the formation of ultracold molecular gases and eventually condensates. As an example we mention LiCs, which represents a flexible system [35]. Its equilibrium internuclear distance and dipole moment in the rovibrational ground state are $R_{eq} = 6.90$ a.u. and $D_{eq} = 2.16$ a.u., indicating an enhanced influence of the electric field on both the rotational and vibrational motions.

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- [1] Y.B. Band and P.S. Julienne, Phys. Rev. A **51**, R4317 (1995).
 [2] T. Takekoshi, B.M. Patterson, and R.J. Knize, Phys. Rev. Lett. **81**, 5105 (1998).
 [3] N. Vanhaecke, W. de Souza Melo, B. Laburthe Tolra, D. Com-

- parat, and P. Pillet, Phys. Rev. Lett. **89**, 063001 (2002).
 [4] H.L. Bethlem, F.M.H. Crompvoets, R.T. Jongma, S.Y.T. van de Meerakker, and G. Meijer, Phys. Rev. A **65**, 053416 (2002).
 [5] H.L. Bethlem, G. Berden, and G. Meijer, Phys. Rev. Lett. **83**,

- 1558 (1999).
- [6] J.D. Weinstein, R. deCarvalho, T. Guillet, B. Friedrich, and J.M. Doyle, *Nature (London)* **395**, 148 (1998).
- [7] L. Santos, G.V. Shlyapnikov, P. Zoller, and M. Lewenstein, *Phys. Rev. Lett.* **85**, 1791 (2000); **88**, 139904 (2002).
- [8] D.S. Petrov and G.V. Shlyapnikov, *Phys. Rev. A* **64**, 012706 (2001).
- [9] M.A. Baranov, M.S. Mar'enko, Val.S. Rychkov, and G.V. Shlyapnikov, *Phys. Rev. A* **66**, 013606 (2002).
- [10] D. DeMille, *Phys. Rev. Lett.* **88**, 067901 (2002).
- [11] P.R. Brooks, *Science* **193**, 11 (1976).
- [12] S. Stolte, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University Press, New York, 1988), Vol. 1, Chap. 25.
- [13] H.J. Loesch and A. Remscheid, *J. Chem. Phys.* **93**, 4779 (1990).
- [14] B. Friedrich and D.R. Herschbach, *Nature (London)* **253**, 412 (1993).
- [15] B. Friedrich, D.P. Pullman, and D.R. Herschbach, *J. Phys. Chem.* **95**, 8118 (1991).
- [16] J.M. Rost, J.C. Griffin, B. Friedrich, and D.R. Herschbach, *Phys. Rev. Lett.* **68**, 1299 (1992).
- [17] P.A. Block, E.J. Bohac, and R.E. Miller, *Phys. Rev. Lett.* **68**, 1303 (1992).
- [18] B. Friedrich, H.G. Rubahn, and N. Sathyamurthy, *Phys. Rev. Lett.* **69**, 2487 (1992).
- [19] P. Schmelcher, L.S. Cederbaum, and U. Kappes, in *Conceptual Trends in Quantum Chemistry*, edited by E.S. Kryachko and J.L. Calais (Kluwer Academic Publishers, Dordrecht, 1994), pp. 1–51.
- [20] A. Slenczka, B. Friedrich, and D. Herschbach, *Phys. Rev. Lett.* **72**, 1806 (1994).
- [21] B. Friedrich and D. Herschbach, *Phys. Rev. Lett.* **74**, 4623 (1995).
- [22] G.R. Kumar, P. Gross, C.P. Safvan, F.A. Rajgara, and D. Mathur, *Phys. Rev. A* **53**, 3098 (1996).
- [23] W. Kim and P.M. Felker, *J. Chem. Phys.* **107**, 2193 (1997).
- [24] J. Ortigoso, M. Rodríguez, M. Gupta, and B. Friedrich, *J. Chem. Phys.* **110**, 3870 (1999).
- [25] H. Sakai, C.P. Safvan, J.J. Larsen, K.M. Hilligsøe, K. Hald, and H. Stapelfeldt, *J. Chem. Phys.* **110**, 10 235 (1999).
- [26] K. von Meyenn, *Z. Phys.* **231**, 154 (1970).
- [27] J. Ortigoso, G.T. Fraser, and B.H. Pate, *Phys. Rev. Lett.* **82**, 2856 (1999).
- [28] C. Chackerian (private communication).
- [29] R. Rydberg, *Z. Phys.* **73**, 376 (1931); O. Klein, *ibid.* **76**, 226 (1932); A.L.G. Rees, *Proc. Phys. Soc. London* **59**, 998 (1947).
- [30] A. Spielfiedel and W.-U. L. Tchang-Brillet (private communication).
- [31] A. Le Floch, *Mol. Phys.* **72**, 149 (1991).
- [32] J.M. Huré and E. Roueff, *J. Mol. Spectrosc.* **160**, 335 (1993).
- [33] H. Herold and H. Ruder, *J. Phys. G* **5**, 341 (1979).
- [34] B. Friedrich and D.R. Herschbach, *J. Phys. Chem.* **103**, 10 280 (1999).
- [35] A. Mosk, S. Kraft, M. Mudrich, K. Singer, W. Wohlleben, R. Grimm, and M. Weidemüller, *Appl. Phys. B: Lasers Opt.* **73**, 791 (2001).