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Ultrafast quantum dynamics:Classical and non-classical description

Our research program includes the investigation of ultrafast quantum dynamics of molecular systems in strong electromagnetic field: (1) in classical description, the molecules are treated in quantum mechanically and the laser light classically; and (2) in non-classical description both the molecules and the light are treated in quantum framework.

Ultrafast quantum dynamics: classical description

The light-induced nonadiabaticity couples in a controllable way the different electronic states of the molecule and depending on the field intensity this coupling can be strong and extremely large in the vicinity of the light-induced conical intersections (LICIs). The nonadiabatic couplings become singular at the LICIs. In contrast to the situation provided by natural conical intersections (CIs) of field-free molecules, the LICI is controllable in the sense that the laser frequency determines its position in nuclear coordinate space and energy and the laser intensity the strength of the couplings. The presence of a CI provides a source for numerous statical and dynamical nonadiabatic phenomena. As is well studied in free polyatomic molecules, the dynamics of the system is highly affected by CIs and becomes strongly nonadiabatic owing to the strong coupling between the nuclei and electrons. Therefore, we investigated the dynamics in the region of laser-induced CI as well.

Concerning dynamics and interference effects due to LICIs, we have studied the impact of the LICI on the photodissociation of several diatomic molecules like LiF and MgH^+ etc. .. The kinetic energy release (KER) spectra and the angular distribution of the photodissociation products were calculated with and without LICIs for different initial conditions and for several different laser parameters and situations. In these comprehensive and rather involved numerical studies, many interesting results have emerged which can be investigated experimentally. Among others, by means of two-dimensional quantum dynamical calculations, it was shown that the additional rotational degree of freedom in the description causes a measurable quantum interference effect due to the very strong nonadiabatic coupling of the electronic, rotational, and vibrational motions. Continuing the analysis of this photodissociation process and studying carefully the obtained results, we found a robust effect in the angular distribution of the photofragments that serves as a direct signature of the light-induced conical intersection, providing undoubted evidence of its existence [1-3].

Electron dynamics in molecules often are strongly coupled to nuclear dynamics. A proper theoretical description of them in polyatomic molecules is a challenge. There are several different approaches where the electron dynamics are treated very accurately, but keeping the nuclear geometry fixed. We present various types of reduced models including five vibrational modes and three electronic states for the pyrazine ($C_4H_4N_2$) molecule in order to investigate the lifetime of electronic coherence in a rigid and neutral system. Using ultrafast optical pumping in the ground state, we prepare a coherent superposition of two bright excited states, and reveal the effect of the nuclear motion on the preservation of the electronic coherence induced by the laser pulse. Our detailed numerical study with quantum dynamics is meant to be realistic for pyrazine over about 20 femtoseconds, and was further extended so as to probe the effect of such approximations on a model system. We show that long-term revivals of the electronic coherence persist up to the picosecond time range even for the most realistic model [4].

We have determined the direct signatures of LICIs on the molecular spectra as well. The theoretical framework and the working equations have been formulated for computing one-photon transitions between field-dressed rovibronic states. By investigating the dressing-field wavelength dependence of the field-dressed spectra for both full- and reduced-dimensional simulations, direct signatures of the LICI in the field-dressed spectrum are identified. These signatures are i) the appearance of new peaks and the splitting of peaks for both absorption and stimulated emission and ii) the manifestation of an intensity-borrowing effect, that is, an increase in the overall peak intensities when the quasienergy of the initial field-dressed state is in the vicinity of the energy position of the LICI. These signatures of the LICI originate from the strong rovibronic coupling in the field-dressed adiabatic electronic states and the nonadiabatic coupling induced by the LICI [5,6]. Very recently, we succeeded to perform similar studies on the polyatomic formaldehyde molecule. Here the existence of several vibrational degrees of freedom enables LICIs to be created without further involving any rotational coordinate. Our results clearly show the direct impact of the LICI on the field-dressed spectra of the H_2CO molecule. It has been argued that the discussed impact can be expected to be generically operative in polyatomics [7-8].

We also investigated the absorption spectra of the cold Na_2 molecule dressed by a linearly polarized standing laser wave with a theoretical model incorporating translational, electronic, vibrational as well as rotational degrees of freedom. To measure the spectra a weak probe laser field is used whose propagation direction is perpendicular to the direction of the dressing field but has identical polarization direction. Although LICIs are present in our model, the simulations demonstrate a very robust absorption spectrum, which is insensitive to the intensity and the wavelength of the dressing field and which does not reflect clear signatures of light-induced nonadiabatic phenomena related to the strong mixing between the electronic, vibrational, rotational and translational motions. However, by widening artificially the very narrow translational energy level gaps, the fingerprint of the LICI appears to some extent in the spectrum [9].

Ultrafast quantum dynamics: non-classical description

We have concentrated on the subject of quantum light-induced nonadiabatic phenomena as well. It is known today that as an alternative to interactions of molecules with intense laser fields, strong light—matter coupling can also be achieved by their confinement in microscale optical or plasmonic nano-cavities. Such systems are usually described in terms of field-dressed or polariton states, which are the eigenstates of the full "molecule + radiation field" system. Nowadays, polaritonic chemistry is a rapidly growing field that provides a novel tool to modify and control chemical structure and dynamics. In our first study we have investigated the rovibronic spectrum of the diatomic Na_2 molecule dressed by quantized radiation field of an optical cavity [10,11]. The formation of LICIs induced by the quantized radiation field was shown for the first time by identifying the robust light-induced nonadiabatic effects in the spectrum. The formation of polariton states in the strong coupling regime was demonstrated, and it was shown how nonresonant couplings lead to an increased absorption in the field-dressed spectrum even before the ultrastrong coupling regime is reached. The strong modification in the rovibronic photoabsorption spectrum via increasing coupling strength carries the changes induced in both the ground state and the upper and lower polaritonic states [10,11].

In the forthcoming work we have succeeded to investigate the impact of quantum light on a polyatomic molecule. We have studied the nonadiabatic phenomena purely induced by quantum light in the formaldehyde (H_2CO) molecule placed in an optical nano-cavity. The study comprises a full-dimensional (6D) and accurate quantum-dynamical description down to a simple one-dimensional (1D) treatment. It has been found that the simplest model which can approximately reproduce the structure of the numerically-exact 6D spectrum is the 2D model. The field-dressed Born-Oppenheimer absorption spectra have been computed as well for the reduced-dimensional 1D and 2D models in order to judge the applicability of the BO approximation [12]. It has been found that this approximation can fail even for a 1D quantum-dynamical treatment of H_2CO irrespective of the value of the coupling strength. This complements previous results claiming that the BO approximation can be used in the strong coupling regime when only one vibrational degree of freedom is taken into account. Analytical considerations fully corroborate our conclusion for a molecule like formaldehyde. More important is our general finding that the BO approximation fails in the presence of LICI, as already present in the 2D model [12,13].

We have discussed some important topological consequences of light-molecule couplings in a cavity as well [14,15]. Moreover, we have also demonstrated that in certain situations the BO approximation supplemented with light-induced geometric-phase terms yields results that are in good agreement with their exact counterparts [16]. This observation is well known from the world of natural nonadiabatic phenomena.

We have demonstrated for a realistic model of a polyatomic molecule (H_2CO) that the time-resolved ultrafast radiative emission of the cavity enables following both nuclear wavepacket dynamics on, and nonadiabatic population transfer between, polaritonic surfaces without applying a probe pulse. The latter provides an unambiguous (and in principle experimentally accessible) dynamical fingerprint of light-induced conical intersections [17].

We have performed numerical simulations to control the nonadiabatic quantum light-induced dynamics by means of LICIs. We could demonstrate the pronounced difference between the the quantum light-induced avoided crossing and the LICI with respect to the nonadiabatic dynamics of the molecule. Moreover, we have discussed the similarities and differences between the classical and the quantum field description of the light for the studied scenario [18].

For ensembles of N molecules, the N − 1 dark states between the two optically active polaritons feature, additionally, so-called collective LICIs, involving the coordinates of more than one molecule are formed. We have studied the competition between intramolecular and collective light-induced nonadiabatic phenomena by comparing the escape rate from the Franck–Condon region of a single molecule and of a molecular ensemble coupled to a cavity mode. In situations where the polaritonic gap would be large and the dark-state decay channels could not be reached effectively, the presence of a seam of light-induced CI between the polaritons facilitates again the participation of the dark manifold, resulting in a cooperative effect that determines the overall non-radiative decay rate from the upper into the lower polaritonic states [19].

The quantum field description of the photon mode allows one to manipulate the light-matter interaction directly in phase space. We have demonstrated the basic principle of coherent control with quantum light on the avoided crossing in LiF molecule. Using a quantum description of light together with the nonadiabatic couplings and vibronic degrees of freedoms opens up alternative perspective on quantum control. We have shown the deviations from control with purely classical light field and how back-action of the light field becomes important in a few-photon regime [20].

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