Conical Intersections Induced by Quantum Light: Field-Dressed Spectra from the Weak to the Ultrastrong Coupling Regimes

Tamás Szidarovszky[a], Gábor J. Halász[b], Attila. G. Császár[a], Lorenz S. Cederbaum[c], Ágnes Vibók[d]

[a]Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös Loránd University and MTA-ELTE Complex Chemical Systems Research Group, H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary, E-mail: tamas821@caesar.elte.hu

[b]Department of Information Technology, University of Debrecen, PO Box 400, H-4002 Debrecen, Hungary

[c]Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, D-69120, Heidelberg, Germany

[d]Department of Theoretical Physics, University of Debrecen, PO Box 400, H-4002 Debrecen, Hungary and ELI-ALPS, ELI-HU Non-Profit Ltd., Dugonics tér 13, H-6720 Szeged, Hungary, E-mail: vibok@phys.unideb.hu

Abstract

As an alternative to interactions of atoms or molecules with intense laser fields, strong light-matter coupling can also be achieved, both for atoms and molecules, by their confinement in microscale optical or plasmonic cavities. A theoretical framework is formulated for investigating the rovibronic spectra of molecules coupled to one mode of the radiation field in an optical cavity. The approach involves the computation of cavity-field-dressed rovibronic states, which are hybrid light-matter eigenstates of the "molecule + cavity radiation field" system, and the computation of transition amplitudes between these field-dressed states with respect to a weak probe pulse. The cavity-field-dressed rovibronic spectrum of Na_2 demonstrates undoubtedly the presence of a "light-induced conical intersection" induced by the quantized radiation field. Dependence of the cavity-field-dressed spectrum on the cavity-mode wavelength as well as on the light-matter coupling strength is investigated [1].

Theoretical background

I. Field-dressed states

(1) Hamiltonian of a molecule interacting with quantized light of the cavity mode [2]

$$\hat{H}_{\rm tot} = \hat{H}_{\rm mol} + \hat{H}_{\rm rad} + \hat{H}_{\rm int}, \quad \text{where}$$

$$\hat{H}_{\rm rad} = \hbar\omega_c \hat{a}^\dagger \hat{a} \quad \text{and} \quad \hat{H}_{\rm int} = -\sqrt{\frac{\hbar\omega_c}{2\epsilon_0 V}}\hat{\mathbf{d}}\hat{\mathbf{e}}\left(\hat{a}^\dagger + \hat{a}\right)$$

(2) For a homonuclear diatomic molecule, the Hamiltonian represented in the basis of two electronic states and the photon number states is

$$\hat{H} = \begin{bmatrix} \hat{T}+V_1(R) & 0 & 0 & g_{12}(R,\theta)\sqrt{2} & 0 & \cdots \\ 0 & \hat{T}+V_2(R) & g_{21}(R,\theta)\sqrt{2} & 0 & 0 & \cdots \\ 0 & g_{12}(R,\theta)\sqrt{2} & \hat{T}+V_1(R)+\hbar\omega_c & 0 & 0 & \cdots \\ g_{21}(R,\theta)\sqrt{2} & 0 & 0 & \hat{T}+V_2(R)+\hbar\omega_c & g_{21}(R,\theta)\sqrt{3} & \cdots \\ 0 & 0 & 0 & g_{12}(R,\theta)\sqrt{3} & \hat{T}+V_1(R)+2\hbar\omega_c & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

$$g_{ij}(R,\theta) = -\sqrt{\frac{\hbar\omega}{2\epsilon_0 V}}d_{ij}(R)\cos(\theta).$$

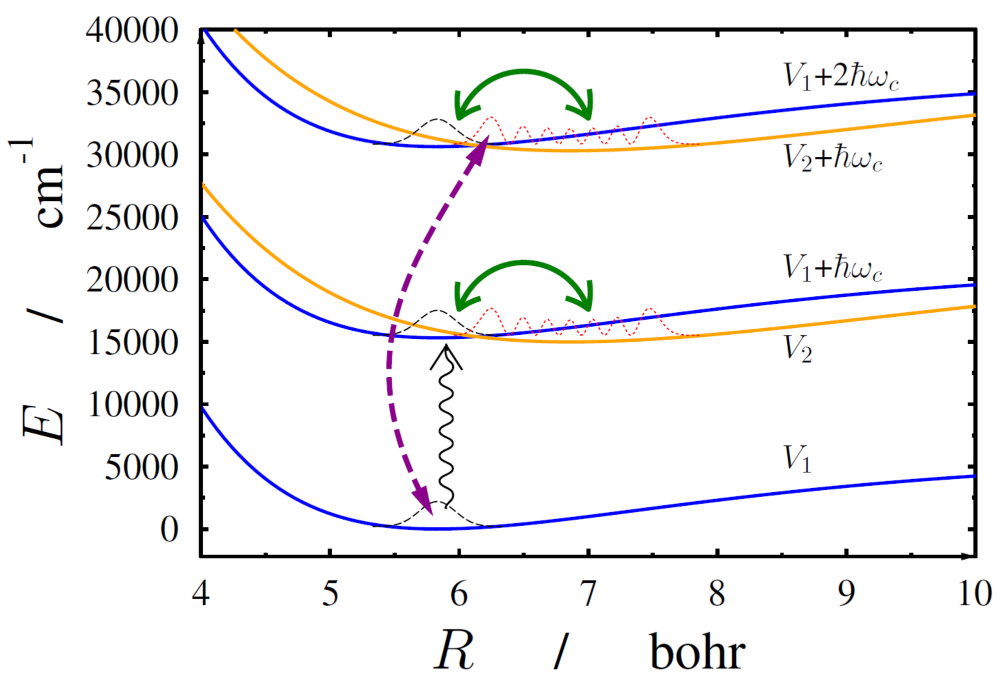

Figure 1. PECs of Na_2 in the cavity, dressed with diferent number of photons of the cavity field, dressing-light wavelength is 653 nm. Vibrational probability densities are drawn for states of |100>|m> type and |261>|m> type. Couplings induced by the cavity radiation field are indicated by the double-headed arrows. The vertical brown wavy arrow indicates transitions between the two manifolds of field-dressed states, resulting form the absorption of a photon of the weak probe pulse.

(3) The field-dressed (FD) states, *i.e.*, the eigenstates of the "molecule + light field" system are obtained by diagonalizing $\hat{H}$ in the basis of field-free

$$\hat{H}_{\rm tot}|\Psi_i^{\rm FD}\rangle = E_i^{\rm FD}|\Psi_i^{\rm FD}\rangle$$

$$|\Psi_i^{\rm FD}\rangle = \sum_{J,v,\alpha,N} C_{i,\alpha vJN}|\alpha vJ\rangle|N\rangle$$

|*N*> is a Fock state with photon number *N*, and |*jvJ*> is a field-free rovibronic state.

II. Transitions between field-dressed states

(4) Let us now compute the absorption spectrum with respect to a weak probe pulse, whose photon number is represented by the letter *M*. Using first-order time-dependent perturbation theory, the transition amplitude of one-photon processes between two field-dressed states is proportional to [2]

$$\langle\Psi_i^{\rm FD}|\langle M|\hat{\mathbf{d}}\hat{\mathbf{E}}|M'\rangle|\Psi_j^{\rm FD}\rangle = \langle\Psi_i^{\rm FD}|\hat{d}\cos(\theta)|\Psi_j^{\rm FD}\rangle\langle M|\hat{E}|M'\rangle \quad \text{where}$$

$$\langle\Psi_i^{\rm FD}|\hat{d}\cos(\theta)|\Psi_j^{\rm FD}\rangle = \sum_{J,v,J',v',N} C^*_{i,1vJN}C_{j,2v'J'N}\langle 1vJ|\hat{d}\cos(\theta)|2v'J'\rangle + \sum_{J,v,J',v',N} C^*_{i,2vJN}C_{j,1v'J'N}\langle 2vJ|\hat{d}\cos(\theta)|1v'J'\rangle$$

[1] T. Szidarovszky, G. J. Halász, A. G. Császár, Lorenz S. Cederbaum, Á. Vibók, *J. Phys. Chem. Lett.*, accepted for publication (2018). arXiv:1808.04797

[2] C. Cohen-Tannoudji, J. Dupont-Roc, G. Grynberg, *Atom-Photon Interactions: Basic Processes and Applications,* Wiley-VCH Verlag GmbH and Co. KGaA, (2004).

Results for the Na_2 molecule

I. Intensity dependence of the FD spectrum

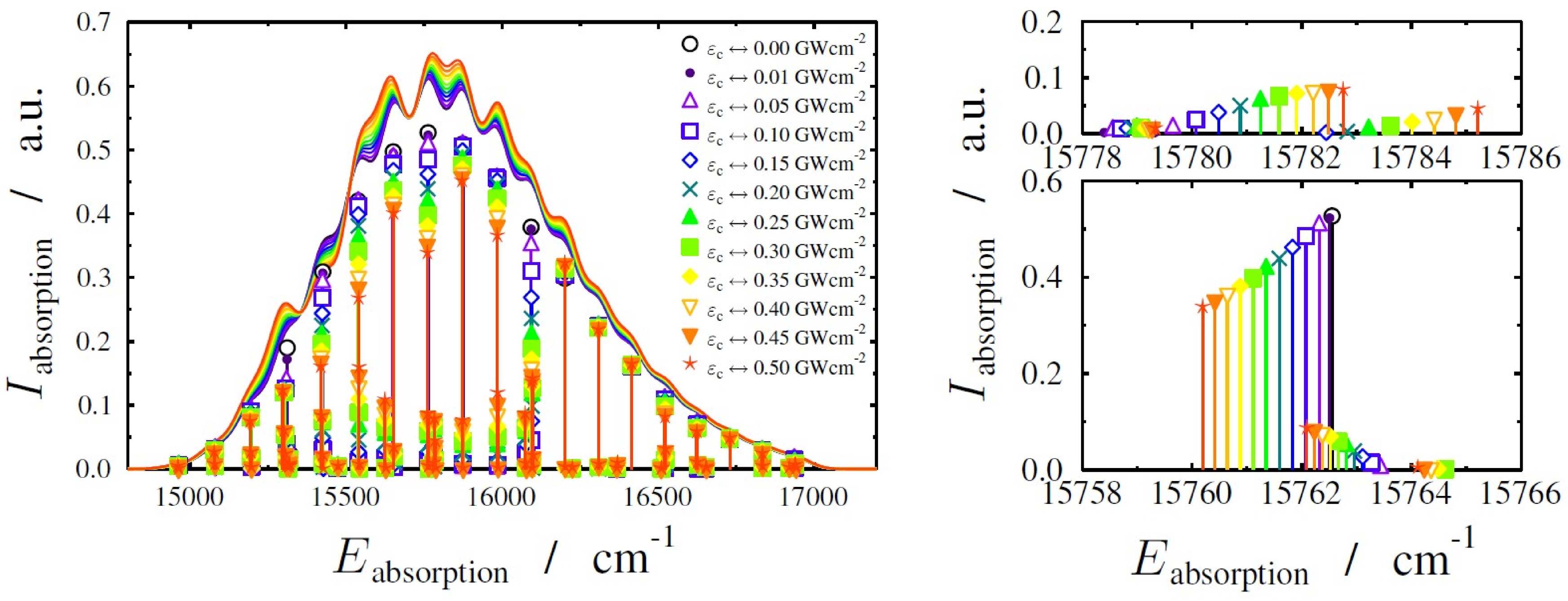

Figure 2. Field-dressed spectra obtained with different values of the light-matter coupling strengths for a cavity mode wavelength of 653 nm. Coupling strength values are indicated by the intensity of a classical light field giving a coupling strength equal to the one-photon coupling of the cavity.

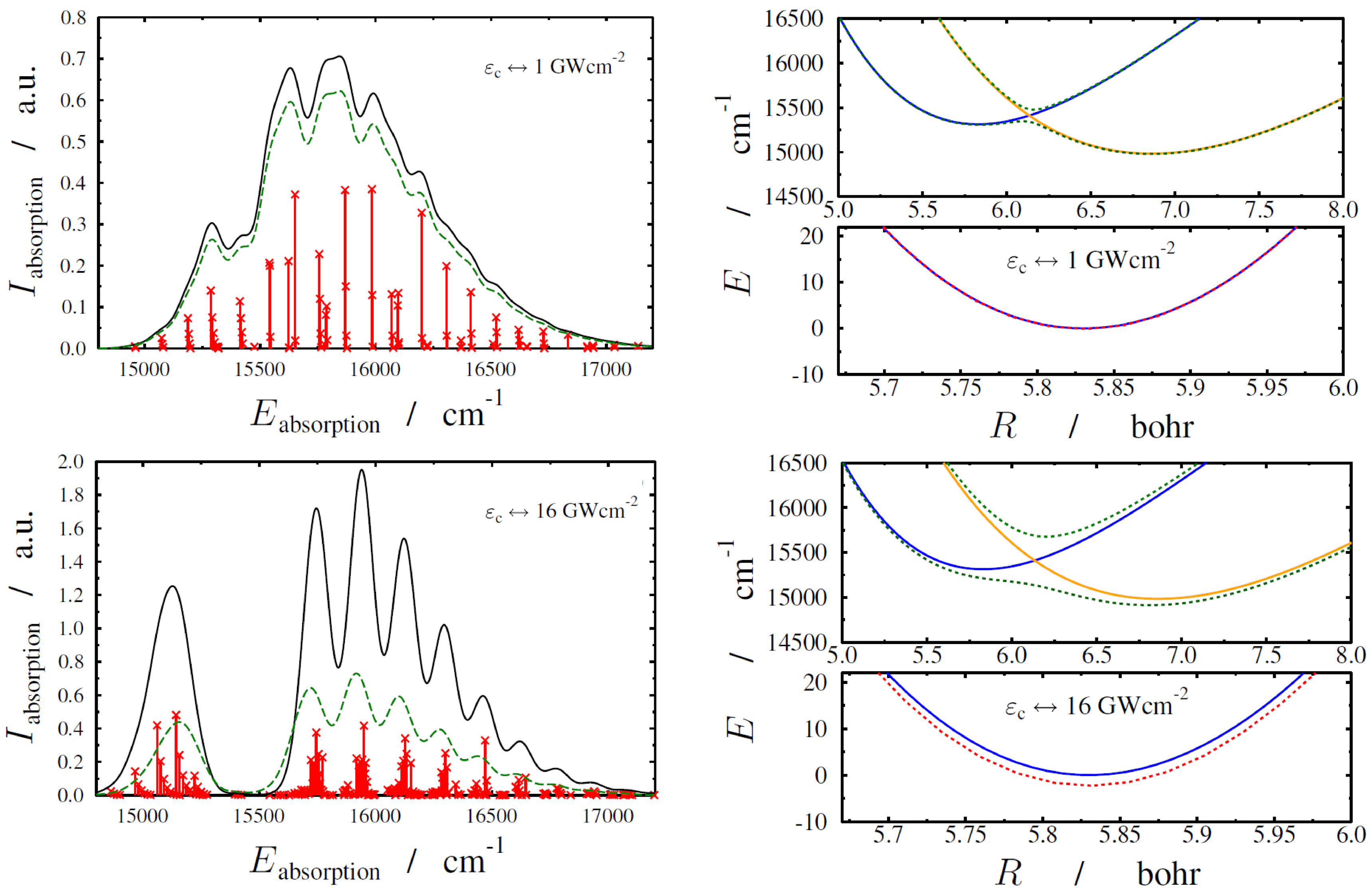

Figure 3. Left column: same as Figure 2, solid and dashed lines correspond to calculations including or excluding the nonresonant couplings in the Hamiltonian, respectively, i.e., the solid and dashed lines refer to using the upper left three-by-three or six-by-six block of $\hat{H}$ respectively. Right column: diabatic and adiabatic PECs at different light-matter coupling strength values.

III. Frequency dependence of the FD spectrum

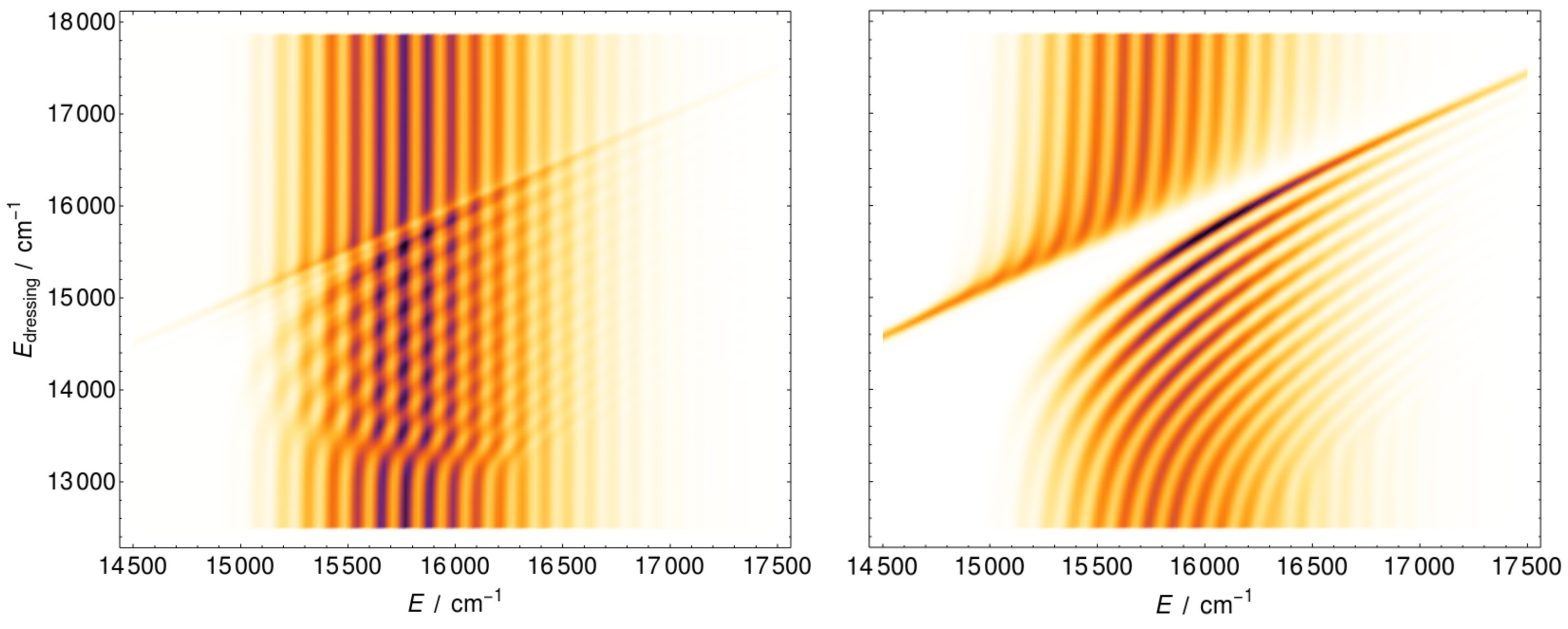

Figure 4. Absorption spectra as a function of the $E_{\rm dressing}$ cavity-mode wavenumber for two cavity one-photon field strengths corresponding to classical field intensities of 1 GWcm-2 (left panel) and 16 GWcm-2 (right panel).

The authors are grateful for the support from EFOP-3.6.2-16-2017-00005, Deutsche Forschungsgemeinschaft (Project ID CE10/50-3) and NKFIH (Grant No. PD124623 and K119658).

HUNGARIAN GOVERNMENT

European Union European Social Fund

INVESTING IN YOUR FUTURE

SZÉCHENYI 2020