

## ON MOLECULAR DISSOCIATION DYNAMICS IN THE PRESENCE OF INTENSE OPTICAL FIELDS

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The final product channel of molecular dissociation is often governed by dynamical behavior near an adiabatic potential surface "avoided crossing". We discuss dynamical switching of the dissociation by field dressing the avoided crossing with an intense, non-resonant optical field. Dissociation of alkali halides in the presence of Nd : YAG or ruby lasers is taken as a specific example.

Inelastic collision processes in the presence of intense, non-resonant radiation have been the subject of theoretical and experimental study since the early seminal work of Yakovlenko [1] and Harris [2]. Energy transfer [3,4], charge transfer [5], and collisional ionization [6–10] have been discussed theoretically and observed in the laboratory. A characteristic common to all these processes is net photon absorption from the applied laser field.

In contrast Lau and Rhodes [11] and George et al. [12,13] have developed theories in which electronic potential surfaces of the collision system are "dressed" by the field so as to distort them from their field-free shape. If this distortion takes place near a potential surface crossing, the dynamics of the collisional interaction may be dramatically altered. The result is a laser-controlled molecular process in which only *virtual* photons are exchanged between the field and the particle system. The control of collisional dynamics near a crossing point is important to a wide range of processes including predissociation, vibronic quenching and excitation, ion-pair production, recombination, and chemical reaction.

We discuss here an application of the Lau–Rhodes theory to two-body dissociation in the context of a simple three-level system illustrated in fig. 1a. A diatomic molecule, ionically bound in the lower energy state, dissociates *adiabatically* to ions by passing through an avoided crossing at fairly large internuclear separation. In effect, interaction between the diabatic levels

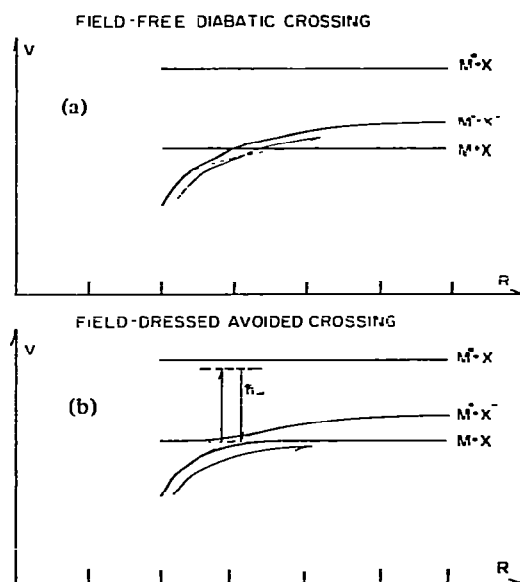


Fig. 1.

is so weak that the active electron does not have time to jump from the neutral to the ionic curve before the system passes through the critical region. However, radiative dipole coupling (via an intense laser field) of each diabatic level to a third, higher-lying level drastically alters the situation. Admixture of this third level introduces a field-dependent off-diagonal matrix element between the two lower diabatic surfaces which

effectively increases the energy gap between the corresponding *adiabatic* surfaces. Fig. 1b shows that as the particle system dissociates through the "field-dressed" adiabatic energy gap, the probability of adiabatic (versus diabatic) dissociation may be greatly enhanced. The effect of the laser on the dissociation dynamics might be gauged by applying the Landau-Zener formula to the relevant field-dressed avoided-crossing parameters [14].

Here we follow a somewhat different though related approach first developed in the pioneering work of Berry and co-workers [15,16]. To make the discussion specific we examine the effect of a Nd:YAG and a ruby laser field on alkali halide dissociation.

According to the Berry criterion, relative probability of diabatic versus adiabatic dissociation is directly proportional to the energy separation of the *diabatic-curve* vibrational states  $E_v$  versus the "adiabatic bandwidth"  $E_{AD}$  of the corresponding *adiabatic* curves, with both  $E_v$  and  $E_{AD}$  evaluated in the region of the crossing point. More succinctly the Berry criterion is expressed by a branching ratio

$$\beta = E_{AD}/E_v. \quad (1)$$

Since the ground electronic state of an alkali halide is essentially an attractive Coulomb well, it is a simple matter to write down the eigenenergies of the relevant diabatic vibrational states as a function of internuclear separation [16]. The adiabatic bandwidth  $E_{AD}$  corresponds to the maximum relative kinetic energy of the dissociating partners which permits them to follow the adiabatic path [16]. A simple equation relates  $E_{AD}$  to the energy gap  $\Delta$  between the adiabatic surfaces,

$$E_{AD} \approx (\pi^2/8e^4)(\Delta^4 R_x^4/\hbar^2)\mu, \quad (2)$$

where  $R_x$  is the diabatic crossing point and  $\mu$  the reduced mass of the system. Thus, if the adiabatic energy gap  $\Delta$  is known,  $E_{AD}$  and  $\beta$  may be evaluated. Tables 1, 2, and 3 show the field-free values of  $\Delta$ ,  $E_{AD}$ , and  $\beta$  respectively for the alkali halides. The Berry criterion predicts adiabatic dissociation for systems with  $\beta \gg 1$  and diabatic dissociation for  $\beta \approx 0$ . Intermediate behavior is expected for  $\beta \approx 1$ . According to table 3, therefore, we expect lithium and sodium bromides and iodides to dissociate adiabatically, the remaining lithium and sodium halides to be intermediate; and all others, with the possible exception of KI, to dissociate diabatically. This expectation appears to be in agreement with what is known experimentally [17].

The most favorable candidates for the study of laser-modified dissociation will be among the intermediate cases where the atomic wavefunction overlap is not so small that an induced radiative interaction between diabatic levels is entirely negligible. We choose NaCl and KI as illustrative examples. The first step is to calculate the adiabatic energy gap  $\Delta_{fd}$  of the field-dressed levels near the crossing point. We apply eqs. (3.20), (3.57) and (3.64) of ref. [11] to this problem and assume a laser field of  $10^{10}$  W/cm<sup>2</sup>. Next, the laser-induced adiabatic bandwidth  $E'_{AD}$  is calculated from  $\Delta$ ,  $\Delta_{fd}$ , and eq. (2). Finally the laser-induced branching ratio  $\beta'$  is determined from  $E'_{AD}$  and the vibrational spacing  $E_v$  of the Coulomb well. The results for NaCl and KI are entered in table 4. The last column shows that a substantial enhancement in the branching ratio may be expected at the 10 GW power level.

These results must be considered only a rough guide because they depend very sensitively on  $\Delta$  and  $\Delta_{fd}$ , neither of which is known with a high degree of accuracy. Calculation of  $\Delta_{fd}$  from the Lau-Rhodes theory is itself uncertain since the dipole transition matrix ele-

Table 1  
Adiabatic energy gaps  $\Delta$  calculated from data in ref. [17]. Entries are in cm<sup>-1</sup>. Values less than 10<sup>-3</sup> cm<sup>-1</sup> are entered as zero

	F	Cl	Br	I
Li	$1.71 \times 10^2$	$1.36 \times 10^2$	$4.88 \times 10^2$	$1.65 \times 10^3$
Na	$6.72 \times 10^1$	$4.00 \times 10^1$	$1.99 \times 10^2$	$8.83 \times 10^2$
K	$1.28 \times 10^{-1}$	$1.91 \times 10^{-1}$	$5.60 \times 10^{-1}$	$2.32 \times 10^1$
Rb	$7.41 \times 10^{-3}$	0	$4.37 \times 10^{-2}$	6.12
Cs	0	0	0	$1.57 \times 10^{-1}$

Table 2

Adiabatic bandwidths  $E_{AD}$  calculated from the adiabatic energy gaps  $\Delta$  of table 1 and eq. (2) which may be conveniently expressed as  $E_{AD} (\text{cm}^{-1}) = (2.726 \times 10^{-12}) [\Delta (\text{cm}^{-1})]^4 [R_x (\text{\AA})]^4 [\mu (\text{amu})]$ . Values less than  $10^{-3} \text{ cm}^{-1}$  are entered as zero

	F	Cl	Br	I
Li	$3.25 \times 10^1$	$2.34 \times 10^1$	$2.51 \times 10^3$	$1.95 \times 10^5$
Na	2.71	$7.73 \times 10^{-1}$	$3.33 \times 10^2$	$7.45 \times 10^4$
K	0	0	0	$3.84 \times 10^{-1}$
Rb	0	0	0	$5.39 \times 10^{-1}$
Cs	0	0	0	0

Table 3

Branching ratio  $\beta$  of adiabatic to diabatic dissociation. Entries calculated from  $E_{AD}$  of table 2,  $E_v$  of table 4 in ref. [16], and eq. (1). Entries of zero indicate values less than  $10^{-2}$

	F	Cl	Br	I
Li	$2.70 \times 10^{-1}$	$2.34 \times 10^{-1}$	$2.09 \times 10^1$	$1.39 \times 10^3$
Na	$3.87 \times 10^{-2}$	$1.49 \times 10^{-2}$	5.84	$1.08 \times 10^3$
K	0	0	0	$1.42 \times 10^{-2}$
Rb	0	0	0	0
Cs	0	0	0	0

ments connecting each crossing level to the higher lying third level must be approximated. For all alkali halides, the third level correlates to an alkali atom in its resonance excited state and the halide atom in its ground state. Since the curve crossings take place at large internuclear separation, where the two partners are only weakly interacting, we take the transition dipole connecting the lower valence state to the third level as essentially equal to the alkali atomic transition moment. The work of Stevens et al. [18] on  $\text{Na}_2$  supports the apparent plausibility of this assumption. The corresponding moment, connecting the ionic curve to the third

level, is almost certainly smaller. We are aware of no calculation of this matrix element as a function of internuclear separation for any of the alkali halides, so we have estimated an *upper limit* to it rather arbitrarily as one half the alkali atomic transition moment. Another rough estimate based on the optical absorption measurements of Davidovits and Brodhead [19] indicates that the relevant transition moment may be closer to one fourth the atomic value.

Despite the uncertainty in  $\Delta$  and  $\Delta_{fd}$  the results of table 4 are qualitatively useful in guiding the choice of systems for study and for design of experiments. For

Table 4

Effect of intense non-resonant field on energy gaps  $\Delta'$ , adiabatic bandwidth  $E'_{AD}$ , and branching ratio  $\beta'$  for two alkali halides. Enhancement of branching ratio by the laser field is given by  $\gamma = \beta'/\beta$

	Laser field (10 GW/cm <sup>2</sup> )	$\Delta_{fd} (\text{cm}^{-1})$	$\Delta' (\text{cm}^{-1})$	$E'_{AD} (\text{cm}^{-1})$	$\beta'$	$\gamma$
NaCl	ruby	40	67.6	6.31	0.12	8.1
KI	Nd : YAG	23.2	30	10.6	0.39	27.5

example, as is evident from figs. 1a and 1b, collisional dissociation from the electronic ground state would result in a prompt *quenching* of ion production and concurrent *increase* in atom production when the laser field is applied. On the other hand photodissociation from the excited electronic state will exhibit exactly opposite effects. Even a qualitative guide to the expected branching ratio enhancement therefore is useful for an optimal choice of detection sensitivity.

Nevertheless an accurate calculation of the off-diagonal elements in the diabatic matrix is required in order to decide the question of experimental feasibility. This is true because 10 GW of laser power is the practical upper limit for an unambiguous experiment. Optical field intensities above this level induce a host of higher order dissociation and ionization pathways which will obscure or even pre-empt the desired effect. Note that an error of 2 in  $\Delta$  or  $\Delta_{fd}$  will propagate in  $E_{AD}$  or  $E'_{AD}$  as a factor of 64 which may well spell the difference between the success or failure of experimental observation. We conclude therefore that reliable and useful application of the Lau–Rhodes theory must be predicated on accurate molecular transition matrix elements at large internuclear separation near the vicinity of the diabatic crossing point.

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