Eur. Phys. J. D **7**, 173–180 (1999)

THE EUROPEAN
PHYSICAL JOURNAL D

EDP Sciences

Vibronic state specific predissociation rates from excited electronic states

H. Hornburger[a] and M. Melzig[b]

Max-Planck-Institut für Quantenoptik, 85748 Garching bei München, Germany

Received: 13 November 1998

Abstract. It is shown that predissociation can be perceived as a primary process due to the continuum part of a Morse oscillator potential. In the model proposed here internal conversion to the ground state is thus not necessarily the primary process of a consecutive dissociation but may be a simultaneous decay. As a consequence, dissociation rates should show strong variations from specific (ro-) vibrational states of the first excited electronic states that are similar to those known from "pure" internal conversion rates. This behaviour is demonstrated by calculating predissociation rates for the $C_6H_6 \rightarrow C_6H_5 + H$ process. Especially the out-of-plane modes seem to play an extraordinary role in the excess energy behaviour of the predissociation rate. At lower excess energies, rates from single vibronic levels with out-of-plane mode characteristics may show an increase by several orders of magnitude.

PACS. 33.50.-j Fluorescence and phosphorescence; radiationless transitions, quenching (intersystem crossing, internal conversion) – 33.80.Gj Diffuse spectra; predissociation, photodissociation

1 Introduction

A general feature of molecules and especially aromatic hydrocarbon molecules is that as the vibrational excess energy increases in the first electronic state, the vibronic bands become broad and diffuse [1]. At the same time, a sharp increase of the nonradiative rates is observed in conjunction with decreasing fluorescence and phosphorescence yields [2,3]. Internal conversion to the ground state is identified as one of the main causes of these effects [4–6]. However, photoisomerization [7,8] and photodissociation [9] have also been thrown into the debate. In a model based on local modes, Lawetz *et al.* [9] analyzed that the predissociation decay and internal conversion could not account for the known three orders of magnitude higher nonradiative decay in benzene. However, as was recently shown [10], the communicating states model provides an adequate increase of the internal conversion rate mainly caused by the out-of-plane modes of that molecule. As in our proposed model the dissociation process for the $C_6H_6 \rightarrow C_6H_5 + H$ is a simultaneous and competing process, it is reasonable to expect that out-of-plane modes increase the dissociation rate by several orders of magnitude, too. Experimental results for predissociation rates investigated with excitation solely at 248 nm showed about 3% of photoproducts [11,12]. Yokoyama *et al.* [11] found preferentially $C_6H_4 + H_2$ products (with a relative yield of 0.96) and $C_5H_3 + CH_3$ (0.04), while the $C_6H_5 + H$ product yield seems to be considerably lower.

The possibility of out-of-plane modes playing an extraordinary role is supported by experiments exploring predissociation of van der Waals molecules. Semmes *et al.* [13] find predissociation of the *t*-stilbene-He complex to be significantly faster from low excess energy out-of-plane vibrations than from higher energy in-plane vibrations. Extreme mode selectivity was also found by Alfano *et al.* [14].

Indications that a very important part in predissociation reactions is played by out-of-plane vibrations in aromatic hydrocarbons were given very early by Hochstrasser *et al.* [15,16].

There is very little work on the variation of predissociation with the quantum numbers of the modes and angular momentum. Vibrational predissociation of triatomic van der Waals molecules was investigated by Beswick and Jortner [17]. This theoretical derivation shows that predissociation of the rare-gas van der Waals atoms can be a highly sensitive function of the vibrational and angular momentum quantum numbers of the nondissociating I-I bond. For high values of the quantum numbers the predissociation rate increases by more than four orders of magnitude. In addition, also the shape of the predissociation rate as a function of the quantum numbers n and l varies considerably if the harmonic I-I bond is replaced by a Morse oscillator potential. However, it may be questionable whether these results obtained for van der Waals bonds with their characteristic low dissociation energies can generally be applied to the very different molecular

---

[a] e-mail: `h.hornburger@mpq.mpg.de`

[b] Sommerstr. 20, 82234 Wessling, Germany

bonds with their several hundred-times higher dissociation energies.

In a further very recent work Choi and Moore [18] look under collisionless conditions for mode specificity in unimolecular reactions of the electronic ground state. In a *résumé* they conclude that most of several qualitatively new features of these HFCO spectra is the existence of sharp unmixed vibrational states at energies far above the dissociation threshold. All of these stable states observed in HFCO are uniquely assigned and found to have extreme excitation in the CH-out-of-plane bending mode and at most one quantum of excitation in the C=O stretch vibration. These extreme motion states are thus proposed to be extremely stable to state mixing and to coexist with a uniform mode mixed quasicontinuum of states for highly excited polyatomic molecules. They argue that mode specificity may be a universal property of all molecules and that it co-exists with nearly statistical dynamics in some energy ranges. Choi and Moore [19] conclude that the strong dependence of the unimolecular reactions on the rotational quantum numbers K and, in the tunneling region, on J and K seems to result from Coriolis coupling of extreme motion in the reaction coordinate to the background levels or directly to the out-of-plane vibration. Isoenergetic states with higher excitations in the out-of-plane bending mode dissociate more slowly than others.

Recently in benzene the influence of CH local modes and particularly the model of "communicating states" on the predissociation rate was investigated [20,21]. These studies suggest that predissociation rates should show, similarly to internal conversion [22], a highly (ro-) vibrationally mode-specific and bond-selective structure. As Coriolis coupling was identified as the most effective coupling mechanism between the modes the decay rates are expected to be additional highly rovibronic specific as well [23]. The aim of this work is to provide predissociation rate calculations from selective single vibronic levels of benzene. These calculations should confirm the hypothesis of state-specific predissociation rates. Approximations entering our model are referred to in detail in previously published work [20,21]. Benzene is taken as an example of aromatic hydrocarbons because of well-known molecular parameters and many experimentally known results.

2 Theoretical considerations

The formalism of the single vibronic level (SVL) rate equation $k_{\mathrm{nr}}(\hat{n})$ has already been derived in reference [20], $\hat{n}$ being in general the set of quantum occupation numbers of the vibrations excited in the electronic state S_1. In the following derivation nonradiative decay, which, as a consequence of the completeness relation, is conceived as the sum of internal conversion and vibrational predissociation, can be expressed by

$$k_{\mathrm{nr}}(\hat{n}) = k_{\mathrm{IC}}(\hat{n}) + k_{\mathrm{VP}}(\hat{n}). \tag{1}$$

For the actual calculation of the nonradiative rate $k_{\mathrm{nr}}(\hat{n})$ one uses the generating function formalism $L_{fi}(t)$ derived in reference [20]:

$$k_{\mathrm{nr}}(\hat{n}) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} L_{fi}(t)\mathrm{d}t = \int_{-\infty}^{\infty} \sum_{\{f\}} |V_{fi}|^2 \ \exp\left[i\frac{E_f - E_i}{\hbar}\ t\right] \mathrm{d}t, \tag{2}$$

where $\{f\}$ denotes the summation of all vibrational occupation numbers of the final electronic state. V_{fi} describes the coupling between initial and final states [24]:

$$V_{fi} \approx V_{fi}(\mathbf{Q}_0) \times \langle \chi_{f,p}\,|\partial/\partial Q_p|\,\chi_{i,p}\rangle \prod_{\mu \neq p}^{N} \langle \chi_{f,\mu}|\chi_{i,\mu}\rangle. \tag{3}$$

The promoting mode is denoted by the subscript p. N is the number of vibrations, while $\chi_{i,\mu}, \chi_{f,\mu}$ are the vibrational wave functions in the initial and final states. $V_{fi}(\mathbf{Q}_0)$ represents the electronic part of the transition matrix element taken at the equilibrium nuclear position $\mathbf{Q}_0$.

The actual evaluation of the integral in equation (2) employs the SVL-generating function of Metz [24] along with the single-saddle-point approximation of Lin [25]. This yields an approximation of the generating function $L_{fi}(t)$ in product terms of SVL-generating functions $Z(t)$ evaluated at the imaginary time $t = -i\tau$:

$$Z(\tau) = |V_{fi}(\mathbf{Q}_0)|^2 \exp\left[\frac{-\Delta E\ \tau}{\hbar}\right] \prod_{\mu=1}^{N} Z_\mu(\tau)\,, \tag{4}$$

where $\Delta E = E_i^0 - E_f^0$ is the pure electronic energy gap.

The rate is then obtained as a function of the saddle-point parameter τ,

$$k_{\mathrm{nr}}(\hat{n}) = \sqrt{2\pi}\ \frac{Z(\tau)}{\left[\langle h^2(\tau)\rangle - \langle h(\tau)\rangle^2\right]^{1/2}}\ \ , \tag{5}$$

where $h(\tau)$ and $h^2(\tau)$ are the first and second derivatives with respect to τ [20]. For harmonic oscillators the $Z_\mu(\tau)$ are straightforward [20]. For the Morse oscillator it is assumed that $Z^{\mathrm{M}}(\tau)$ can be conceived as the sum of internal conversion (only the discrete states) $Z_{\mathrm{IC}}^{\mathrm{M}}(\tau)$ and vibrational predissociation (only the continuum states) $Z_{\mathrm{VP}}^{\mathrm{M}}(\tau)$ contributions:

$$Z^{\mathrm{M}}(\tau) = Z_{\mathrm{IC}}^{\mathrm{M}}(\tau) + Z_{\mathrm{VP}}^{\mathrm{M}}(\tau)\,. \tag{6}$$

Equation (1) is thus a direct consequence of equation (6).

Explicitly, the most general form of the SVL-generating function for the Morse oscillator $Z^{\mathrm{M}}(\tau)$ is

$$Z^{\mathrm{M}}(\tau, n) = \sum_{m=0}^{m_{\max}} |\langle \chi_m(q)|\chi_n(q)\rangle|^2 \times e^{-\frac{\tau}{\hbar}(E_n - E_m)} + \frac{1}{2\pi^2 k_f} \int_0^{\infty} e^{-\frac{\tau}{\hbar} p_f^2 \kappa_f} \times |\langle \chi_{p_f}(q)|\chi_n(q)\rangle|^2 e^{-\frac{\tau}{\hbar}E_n} \mathrm{d}p_f, \tag{7}$$

this equation referring to excitation of discrete vibrational states n. $\chi_n(q), \chi_m(q)$ and $\chi_{p_f}(q)$ are the one-dimensional normalized Morse oscillator wave functions for the bound and scattered states, respectively.

The wave functions and anharmonic constants for Morse oscillator potentials are taken from earlier work [26]. Matrix elements for discrete-discrete transitions as well as those for discrete-continuum transitions and, furthermore, the derivatives of $Z^{\mathrm{M}}(\tau, n)$ are already derived in reference [20].

However, equation (6) describes the situation for a single Morse oscillator within the basis set of vibrations of a certain molecule. Often several Morse oscillator potentials and generally $N_{\text{anh.}}$ different potentials with discrete and continuum regions occur and thus one gets a considerably more complicated version of equation (6) with a general mixing of continuum and discrete terms:

$$Z^{\text{anh}}(\tau) = \prod_{j=1}^{N_{\text{anh.}}} \left[Z_{\text{IC}}^{\text{anh}}(\tau, j) + Z_{\text{VP}}^{\text{anh}}(\tau, j) \right]. \tag{8}$$

In benzene, at least the ν_1 and the six CH-local modes are assumed to have potentials of the Morse oscillator shape. Consequently, each is of the form given for $Z^{\mathrm{M}}(\tau, n)$ in equations (6) and (7).

The components of $k_{\text{nr}}(\hat{n})$ should be related to the total singlet decay rate $k_{S_1}(\hat{n})$ from the excited state (here the singlet excited state S_1). $k_{S_1}(\hat{n})$ is composed of the radiative rate $k_{\text{r}}(\hat{n})$, the intersystem crossing rate $k_{\text{ISC}}(\hat{n})$, the internal conversion rate $k_{\text{IC}}(\hat{n})$, and, finally, the vibrational predissociation rate $k_{\text{VP}}(\hat{n})$:

$$k_{S_1}(\hat{n}) = k_{\text{r}}(\hat{n}) + k_{\text{ISC}}(\hat{n}) + k_{\text{IC}}(\hat{n}) + k_{\text{VP}}(\hat{n}). \tag{9}$$

Furthermore the vibrational predissociation quantum yield $Q_{\text{VP}}(\hat{n})$ is given by

$$Q_{\text{VP}}(\hat{n}) = k_{\text{VP}}(\hat{n}) / k_{S_1}(\hat{n}). \tag{10}$$

The electronic matrix element $V_{if}(\mathbf{Q}_0)$ is assumed to be nuclear independent. From this hypothesis follows that $|V_{if}(\mathbf{Q}_0)|^2$ can be treated as a constant and its value is of no relevance for the present study. It seems therefore useful to define a solely Franck-Condon dependent normalized rate $k_{\text{nr}}^{'}[\text{cm}^2/\text{s}]$,

$$k_{\text{nr}}^{'}(\hat{n}) = k_{\text{nr}}(\hat{n}) / [|V_{fi}(\mathbf{Q}_0)|^2 \; k_0], \tag{11}$$

where $k_0 = 10^{-17}$.

3 Results and discussion

In the following, calculations are presented for predissociation rates of H atoms when several single vibronic levels are excited. For detailed discussions about assumptions and restrictions of the model we refer to references [20] and [21]. For the CH- and CD-stretch vibrations we assume the concept of local modes with parameters $\kappa = 55.2$ (31.7) cm^{-1}, $\Delta q = -0.01143$ Å, $\omega_i = 3273$ (2433.3) cm^{-1}, $\omega_f = 3183$ (2366.4) cm^{-1}, while the energy gap for the S_1 state is $\Delta E = 38086$ (38289) cm^{-1}. These anharmonic parameters result in a dissociation barrier of the local modes in the final ground state at $D = 45885$ (44163) cm^{-1} and its isoenergetic value in the S_1, $E_{\text{ex}} = 7799$ (5874) cm^{-1}, as obtained by spectroscopically found anharmonicity parameters, while the thermodynamically obtained value is $D = 38761$ cm$^{-1} \hat{=} E_{\text{ex}} = 675$ cm^{-1}. For the ν_1 total symmetric CC-stretch vibration, for the $\nu_4(b_{2g})$ out-of-plane mode as well as for all remaining vibrations harmonic oscillator potentials are assumed [27].

Predissociation rates for H-atoms from progressions of the CH-stretch vibration ν_2 have already been determined in an earlier SVL- calculation. These results should now be completed by the predissociation rates of H-atoms, when single vibronic levels of the CC-stretch vibration ν_1 and the out-of-plane mode ν_4 are excited. It has to be mentioned, that these modes are not directly coupled to the local mode CH-stretch vibrations with Morse potentials. In the model calculations it is assumed that all these modes have harmonic and thus nondissociative potentials. However, as will be seen in the following, their influence on the predissociation rate of a hydrogen atom is much stronger than exciting directly levels of the CH-stretch vibration with its dissociative potential. The out-of-plane mode ν_4 has the strongest distortion of all modes and for supposed harmonic potentials the lowest crossing point of the multidimensional potential surfaces of the S_1 and S_0 electronic states. On the increase of the "total nonradiative rate" with excess energy it exerts by far the strongest influence of all the out-of-plane modes and is therefore the best representative of this species of modes in benzene. Most known experimental results of decay processes from the S_1 involve progressions of the ν_1.

To allow an easy comparison of theoretical and experimental results, therefore, predissociation rates should especially be calculated from levels with ν_1 participation.

By selecting these three characteristic modes with their different properties it is hoped to demonstrate the main features dominating the SVL-dependent predissociation rate calculation. In Figure 1 the SVL rates for progressions of the ν_1, ν_2 and ν_4 are compared. The predissociation rates obviously show a strong mode specificity. Generally, the rates increase with higher occupation numbers. For $n_1 = 4$ of the ν_1 at about $E_{\text{ex}} \approx 3700$ cm^{-1} the rate is one order of magnitude higher than that at zero excess energy. Quite different from this result, for the ν_2 one obtains at an excess energy of ≈ 3000 cm^{-1} even a slightly lower value than that found at the origin, being expressed by a factor ≈ 0.86. However, the small decrease might also be a consequence of the local mode approximation proposed by Henry *et al.* [28]. The ν_2 mode shows in the whole investigated energy range only an increase of a factor ≈ 1.2 (≈ 2.2 for C_6D_6 for $n = 6$ at $E_{\text{ex}} = 11215.5$ cm^{-1}). The much stronger increasing rates in reference [20] have been obtained by inconsistent quantum numbers for the local modes in the excited electronic state. The predissociation rates obtained, however, when

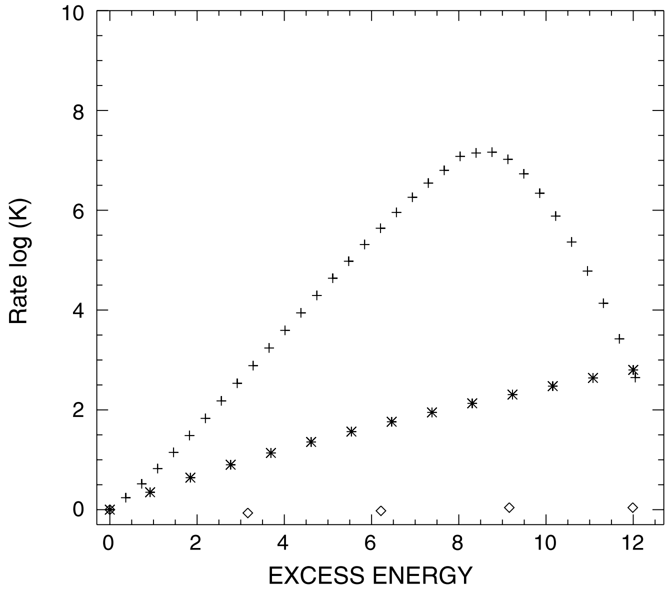

Fig. 1. Relative dissociation rates for the $C_6H_6 \rightarrow C_6H_5 + H$ process $K = k_{\mathrm{VP}}\ (E_{\mathrm{ex}})/k_{\mathrm{VP}}(E_{\mathrm{ex}} = 0)$ as a function of progressions of the ν_1 (stars), ν_2 (diamonds) and ν_4 (crosses). Excess energy $E_{\mathrm{ex}}[\times 1000\ \mathrm{cm}^{-1}]$ in the S_1 state.

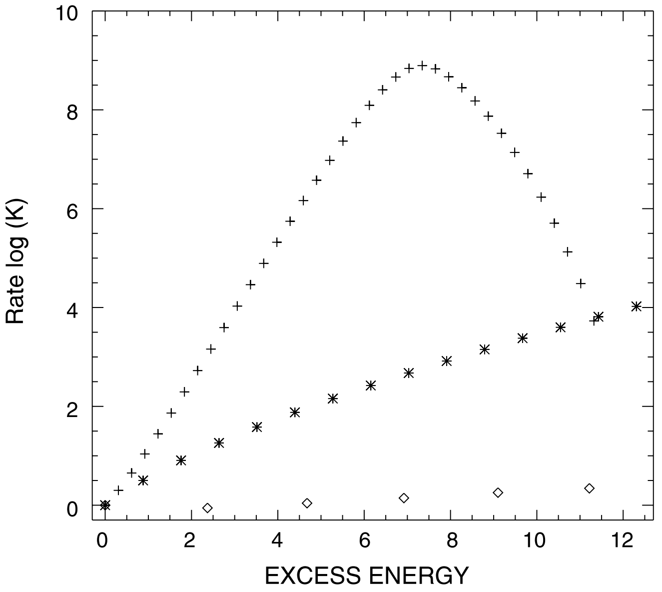

Fig. 2. Relative dissociation rates for the $C_6D_6 \rightarrow C_6D_5 + D$ process $K = k_{\mathrm{VP}}(E_{\mathrm{ex}})/k_{\mathrm{VP}}(E_{\mathrm{ex}} = 0)$ as a function of the progressions of the ν_1 (stars), ν_2 (diamonds) and ν_4 (crosses). Excess energy $E_{\mathrm{ex}}[\times 1000\ \mathrm{cm}^{-1}]$ in the S_1 state.

levels of the ν_2 vibration are excited agree quite satisfactorily with experimental results.

The majority of the experiments, performed so far, are based on the assumption of non-ro-vibronic-selective predissociation rates. The experimental set-up was therefore mostly not suitable to detect selectivity. Therefore an almost constant, excitation energy independent predissociaton rate in a large excess energy range was detected.

Most remarkable, however, is the increase of the calculated rates when levels of the out-of-plane mode ν_4 are excited in the S_1. At $\approx 3000\ \mathrm{cm}^{-1}$ ($n_4 = 8$) the calculated predissociation rate increases by a factor ≈ 2–3×10^2. Extraordinarily for this mode one finds, furthermore, a maximum relative rate $K \approx 10^7$ at $E_{\mathrm{ex}} = 8760\ \mathrm{cm}^{-1}$ ($n_4 = 24$) surprisingly followed by a steep decrease with still higher occupation numbers. This special behaviour, only found for the ν_4 out-of-plane mode, disagrees remarkably with the increase of the rates for the totally symmetric vibrations ν_1 and ν_2. For these modes the slopes are slightly concave or flatten for higher excess energies. Naturally one should mention, that experimentally realized spectra at most find levels with quantum numbers $n_4 = 6$. It is obvious that experimentally the $n_4 = 24$ line cannot be found, because of the strong spectral broadening caused, *e.g.*, by the "channel three" effect and general couplings etc. In experimental reality, at high excess energies in a broad band many other modes would be coupled to the ν_4 mode. Further the ν_4-mode may be anharmonic.

However, one may assume that at this higher excess energies, the predissociation rate of an excited broad band containing many coupled levels is in most cases governed, above all, by the behaviour of the out-of-plane modes. Thus it seems realizable to find regions of strong increases of the rate depending on the coupling of the ν_4 to the remaining states in the band. The slope for the ν_4 dissociation SVL-rates is therefore an "optimal" rate curve at high excess energies.

In perdeuterated benzene (see Fig. 2) the increase of the rates is still higher for all modes and, as compared with C_6H_6, leads in the case of the ν_4 at an excess energy of $\approx 3000\ \mathrm{cm}^{-1}$ to a difference of four orders of magnitude.

In the case of C_6D_6, however, the maximum of the slope of the SVL-decay rate for the ν_4 is located about $1750\ \mathrm{cm}^{-1}$ lower than for C_6H_6. Furthermore if one compares the rate-maxima, a more than two orders of magnitude higher rate is found for C_6D_6. Figures 1 and 2 obviously demonstrate that predissociation should show a strong SVL dependence and furthermore a considerable heavy-atom effect. In the case of the out-of-plane modes one finds surprisingly ambivalent behaviour. At low excess energies the strongest increase is expected to be caused by the out-of-plane modes. For high excess energies, however, these modes —as is well known— greatly contribute simultaneously to the steep enhancement of the nonradiative transitions via the internal conversion channel. This process competes so strongly that at a certain excess energy (in Fig. 1 at $E_{\mathrm{ex}} \approx 14000\ \mathrm{cm}^{-1}$) the predissociation rate falls below the value it obtains at zero excess energy.

A very remarkable property is, however, the approximately exponential increase of all the rate curves (for the ν_4 naturally only below the maximum).

In the real molecule one additionally has a variety of couplings (*e.g.*, communicating states). Nonsmooth behaviour caused by various strong Fermi resonances and/or by rotational J and K dependences is expected to modulate the predissociation rates severely [29]. Thus, the curves in Figures 1 and 2 just show the qualitative trend for the different modes.

The dissociation barriers are calculated from anharmonic constants. These anharmonic values are obtained from an analysis of the first few levels of the vibrational progressions in the S_0 ground state. It is well known that the prediction of the barrier height can thus be about 20% off. Actually, the experimental value for the endothermicity of the CH-bond in benzene is found to be 110.8 cal/mol $\hat{=} 38761$ cm^{-1}, *i.e.* ≈ 7123.5 cm^{-1} below the calculated value obtained from spectroscopic constants [21]. Thus in S_1 benzene rovibronic levels beyond ≈ 800 cm^{-1} of excess energy lie above the effective experimental dissociation barrier of the CH-stretch local mode with Morse potentials in the S_0 ground state.

To evaluate the Franck-Condon factors one also needs the vibrational anharmonic constants for the excited state S_1. However, the anharmonic parameters for these vibrational potentials are largely unknown. Spectroscopically only a few progressions can be measured for most modes. Higher levels are often considerably broadened by couplings to the various remaining levels. Thus one is forced to introduce some reasonable assumptions. The calculations of Lawetz *et al.* [9] have shown that the variation of the initial state S_1 anharmonic constants has only a relative small effect on the values of the matrix elements. Obviously this is due to the low occupation numbers in the initial state S_1 which enter the calculations of the Franck-Condon matrix elements. Although it is a crude approximation, the anharmonic constants in the S_0 and S_1 are assumed to be equal.

This choice is advantageous, however, as it allows to derive analytic expressions for the Franck-Condon factors and to avoid the large numerical errors which enter numerical evaluations of Franck-Condon factors with different anharmonicities.

A very important point not discussed so far is the interpretation of the predissociation rate below and above the "dissociation barrier". The predissociation rate, contrary to the classical concept, shows no influence of the dissociation barrier on the predissociation rate curve. A similar result was already obtained earlier by Waite and Miller [30–33]. In reference [33] Waite and Miller furthermore demonstrated that for the effective potential a barrier is not necessary (*e.g.*, for a Morse potential) and that this "pseudo-barrier" can be treated similar as a real tunneling case. Predissociation in excess energy regions below the dissociation barrier of molecules is obviously due to "quasi-tunneling processes" [33–38].

According to Miller the microcanonical distribution relevant to the molecular case causes tunneling effects in an isolated molecule [32]. These tunneling conditions are especially satisfied when the environment of the molecules can supply the energies within the timescale of the predissociation. This can especially be the case without any presupposition in fluids, at higher pressures in gases, when molecules are generally bound to a reservoir and especially for large molecules with many degrees of freedom.

As has just been discussed, the model calculations use parameters which result in ≈ 7000 cm^{-1} higher barrier values than are shown by experiments. This fact, however, has just a negligible influence on the essential characteristics of the results. Calculations using data which reproduce the correct experimental dissociation barrier show almost the same shape for the predissociation rate. Especially the maxima of the predissociation rates for ν_4 progressions remain almost unshifted.

The only remarkable point is that the contribution of the predissociation rates to the total nonradiative rate approximately doubles for almost all calculated SVL-rates. These results lead unambiguously to a further conclusion. The seemingly obvious correlation (see Figs. 1 and 2) of dissociation limit and maxima of the ν_4 progressions subsequently proves to be accidental. The shape of the dissociation rate curves generally shows to be predominantly a characteristic function of the frequencies, displacements, energy gap and anharmonicities (local modes) in a molecule. Furthermore considerable variations of the local mode anharmonicities, at least for benzene ($\approx 25\%$), show almost negligible effects on the shape of the predissociation rate curve with respect to the S_1 excess energy behaviour. Therefore in the model under consideration the characteristic features prove to be very sturdy with respect to the variation of anharmonic parameters.

Only in the case where the ratios of the rates of intersystem crossing, internal conversion and predissociation as functions of the excess energy in the S_1 state are discussed is the experimentally exact value of the dissociation barrier necessary.

According to the model proposed in this work, mode-specific predissociation rates are caused by excitation of different discrete (ro-) vibronic states in the S_1. This rate is solely and exclusively a function of the Franck-Condon factors. Neither in the initial excited state S_1 nor in the final state S_0 special couplings of the vibrations are assumed. In the final S_0 a uniform, mode-mixed quasicontinuum of states is assumed. The excitation of the specific modes and specific levels in the S_1, respectively, leads to extrem different nascent energy redistributions in the S_0. In the rate equation (2) this ultrashort status is largely determined by the statistical weight of the Franck-Condon factors. This "primary" mode specificity is modulated by many "secondary" effects, *e.g.*, Coriolis-, Fermi-, electronic nonadiabatic- coupling etc. A special case of "secondary" effects is also the variation of the level densities and level widths in the final states, which especially occurs for small molecules, *e.g.*, for HFCO. As a consequence one has to take into account the possibility of incomplete intramolecular vibrational redistribution.

Generally the out-of-plane modes seem to play a most critical role.

In Table 1 the rates and corresponding percentages of internal conversion and dissociation rates are given. Table 2 shows how the energy, electronic plus vibrational excess energy, is redistributed into vibrational energy of the final state just after the transition. This energy distribution has to be regarded as an ultrashort and artificial status since the saddle-point approximation implies highly communicating final states. Nearly at once the energy should be redistributed further into a final thermal

Table 1. Single vibronic level rates $k_{\mathrm{nr}}^{'}(E_{\mathrm{ex}})$ from progressions of the ν_4. Additionally the corresponding percentages of internal conversion $k_{\mathrm{IC}}(\hat{n})$ and CH-dissociation rates $k_{\mathrm{VP}}(\hat{n})$ are given.

n_4^i	E_{ex} (cm^{-1})	$k_{\mathrm{nr}}^{'}(\hat{n})$	k_{IC} (%)	$k_{\mathrm{CH-Diss.}}$ (%)
0	0.0	1.7	90.6	9.1
3	1095	13.2	91.7	8.0
5	1825	68.9	92.6	7.2
7	2555	394.2	93.4	6.4
10	3650	5.8×10^{3}	94.7	5.2
12	4380	3.6×10^{4}	95.5	4.4
14	5110	2.3×10^{5}	96.3	3.6
17	6205	3.6×10^{6}	97.5	2.5
20	7300	5.9×10^{7}	98.5	1.5
23	8395	1.0×10^{9}	99.4	0.6
26	9490	1.9×10^{10}	99.9	0.1
28	10220	1.0×10^{11}	99.995	0.0049
31	11315	7.4×10^{11}	99.99998	0.00002

Table 2. For the single vibronic level rates from progressions of the ν_4 (see Tab. 1) the corresponding percentages of the total energy which the local modes and the ν_4 have accepted just after the nonradiative transition to the S_0 are presented. Additionally the energy accepted by the ν_4 in the S_0 and the corresponding approximated occupation numbers are calculated.

n_4^i	$E(\nu_{\mathrm{loc.m.}}^f)$ (%)	$E(\nu_4^f)$ (%)	$\langle n_4^f\rangle$	$E(\nu_4^f)$ (cm^{-1})
0	91.0	4.2	2	1598
3	79.0	13.2	7	5161
6	66.1	26.4	15	10612
9	54.0	38.7	23	15999
12	42.8	50.2	30	21302
15	32.3	60.9	38	26511
18	22.7	70.8	45	31599
21	13.9	79.7	52	36477
24	6.7	87.3	58	40897
27	2.6	91.9	62	44058
29	1.8	93.2	64	45357
30	1.5	93.7	65	45932
33	0.8	94.8	67	47544

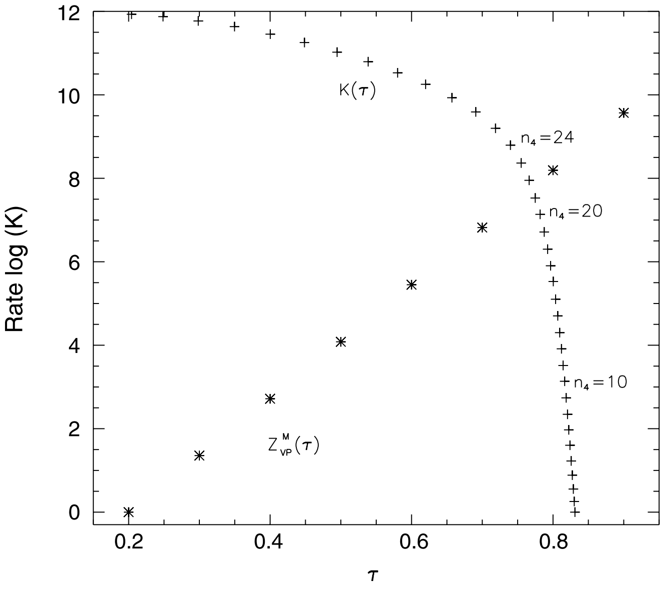

Fig. 3. Relative dissociation rates for the $C_6H_6 \rightarrow C_6H_5 + H$ process $K = k_{\mathrm{VP}}(E_{\mathrm{ex}})/k_{\mathrm{VP}}(E_{\mathrm{ex}} = 0)$ of the ν_4 (crosses) and $Z_{\mathrm{VP}}^{\mathrm{M}}(\tau)$ (Eq. (6)) (stars) as a function of the correlation parameter (saddle-point parameter) τ.

distribution status which is very different from the Franck-Condon-weighted redistribution status, characterized by its "negative temperature". To give further insight the energy which is accepted by the ν_4 and the corresponding approximated occupation numbers $\langle n_4^f\rangle$ in the S_0 are calculated. This ultrashort status, however, just after the transition, is the doorway state and necessary condition for observing selective predissociation. If predissociation is initiated within a timescale shorter than the intramolecular vibrational energy randomizes one should expect SVL-selective predissociation. It can be clearly deduced that the ν_4 out-of-plane mode plays a crucial role. However, the mechanism which explains the sudden drop from high CH-predissociation rates, when the energy accepted by the ν_4 in the S_0 reaches approximately the value of the dissociation energy barrier of the local modes, is only difficult to interpret. In both excess energy regions the out-of-plane modes prevent the energy from flowing into the reaction coordinate and especially into the CH-stretch vibration.

Thus it is obvious that beyond the energy acceptance behaviour some further criteria should enter the considerations. A closer analysis shows that the variation of $Z_{\mathrm{VP}}^{\mathrm{M}}(\tau)$ with the correlation parameter τ (saddle-point parameter) explains most of the shapes of the dissociation rates as a function of the excess energies in Figures 1 and 2. As is shown in Figure 3 $Z_{\mathrm{VP}}^{\mathrm{M}}(\tau)$ increases almost exponentially with τ. τ varies only slightly with the quantum numbers of the ν_1 and ν_2 in the S_1. Thus the value of $Z_{\mathrm{VP}}^{\mathrm{M}}(\tau)$ is almost constant and the main variations must be due to all remaining modes. For higher values of the ν_4, however, this mode accepts more than 90% of the energy and thus the behaviour of this mode dominates the value of τ.

The total nonradiative rate curve for high quantum numbers of the ν_4 shows that τ is strongly decreasing, especially for quantum numbers $n_4 > 24$, where in Figure 1 the maximum of the dissocation rate curve is found. The strong decrease of τ for still higher quantum numbers is the reason for the decrease of the dissociation rate for the ν_4 progressions in Figure 1. Therefore the main mechanism at work is revealed.

The results in Figures 1 and 2 are obtained by assuming a uniform, mode-mixed quasicontinuum of states in the final S_0. To prove, whether these results can be generalized, also for HFCO predissociation rates on the assumption of a mode-mixed quasicontinuum of states in the final

S_0 were calculated [39]. In fact a similar behaviour as for benzene was found. Especially the characteristic decrease of the rate for progressions of the out-of-plane mode can be confirmed, however, the maximum occurs at much lower excess energies (at $\approx 3000\,\mathrm{cm}^{-1}$ excess energy). The predissociation rate decreases in favour of internal conversion.

The predissociation rate from states with high values of the occupation number of the out-of-plane modes, according to Choi and Moore [18,19], is lowered, because these states are assumed to be extremely stable to state mixing, although they are in energy regions of a dense quasicontinuum. Contrary to Moore's interpretation, however, our result would offer, as an explanation, a very general mechanism responsible for the observed effects. Especially the requirement of isolated regions within a dense quasicontinuum for states with high quantum numbers of the out-of-plane modes, according to our explanation, can be completely dropped.

A definite prognosis for the CH predissociation behaviour is only possible if the remaining, at least two, known predissociation processes [6,11] are implemented into the decay formalism of equations (1) and (2). One may expect ro-vibrational level dependent predissociation rates for the remaining products similar to these for the $C_6H_6 \rightarrow C_6H_5 + H$ process. As a further consequence, the relative product rates should therefore strongly vary with the single rovibronic levels excited, too.

Finally one should mention that very recently also several extensive numerical studies have been performed [8, 40–43]. These *ab initio* calculations tried to find the "reaction coordinate" and/or to demonstrate that nonadiabatic conical intersections control the nonradiative transition processes. However, the calculations predominantly present static results, *e.g.*, the form of the multidimensional potential surfaces. Beside the fact that for larger molecules (*e.g.*, benzene) still several restricting assumptions are necessary to guarantee numerical access, dynamical studies are largely unknown. Furthermore, as a consequence of these calculations one had to expect strong anharmonicities of the vibrations in the "channel-three" region. The largely harmonic frequencies which are factually experimentally found even for high quantum numbers of, *e.g.*, the out-of-plane modes and the total symmetric ν_1 CC-stretch vibration seem to highly contradict these numerical results.

4 Conclusions

Relative predissociation rates from progressions of the ν_1, ν_2 and ν_4 of benzene and perdeutero-benzene are calculated. For higher excess energies in the S_1 state the rates from the various progressions differ by several orders of magnitude. Thus a strong single vibronic level dependence of the predissociation rate should occur. Furthermore, a clear perdeuteration effect is shown by the calculations. Over extensive excess energy regions in the S_1 state the out-of-plane mode ν_4 exerts by far the strongest influence of all modes on the variation of the relative predissocation rate for the $C_6H_6 \rightarrow C_6H_5 + H$ process. The most spectacular effect is, however, that a steep decline of the envelope for the rate curve of the ν_4 progressions is found at very high excess energies. Since for very high excess energies in S_1 a general coupling situation is assumed to occur (high level densities, "communicating states model" and especially Coriolis coupling in the S_1), a strong decline of the predissociation rate from almost all vibrational levels is predominantly caused by coupling to this out-of-plane mode.

The authors acknowledge stimulating discussions with F. Metz and S.F. Fischer. The authors also wish to thank the referees for their very helpful comments.

References

1. A.E.W. Knight, C.S. Parmenter, M.W. Schuyler, J. Am. Chem. Soc. **97**, 1993, 2005 (1975).
2. J.H. Callomon, J.E. Parkin, R. Lopez-Delgado, Chem. Phys. Lett. **13**, 125 (1972).
3. L. Wunsch, H.J. Neusser, E.W. Schlag, Z. Naturforsch. A **36**, 1340 (1981).
4. J.L. Knee, C. E. Otis, P. M. Johnson, J. Chem. Phys. **81**, 4455 (1984).
5. U. Schubert, E. Riedle, H.J. Neusser, E.W. Schlag, J. Chem. Phys. **84**, 6182 (1986).
6. K. Yoshihara, "*Dynamic studies on excited benzene*"; Myodaiji, Okazaki 444, Japan (Booklet, Inst. for Mol. Science 1985).
7. A.L. Sobolewski, J. Chem. Phys. **93**, 6433 (1990); A.L. Sobolewski, W. Domcke, Chem. Phys. Lett. **180**, 381 (1991); A.L. Sobolewski, E.C. Lim, W. Siebrand, Int. J. Quant. Chem. **39**, 309 (1991).
8. S. Kato, J. Chem. Phys. **88**, 3045 (1988).
9. V. Lawetz, W. Siebrand, G. Orlandi, Chem. Phys. Lett. **16**, 448 (1972).
10. H. Hornburger, H. Schröder, J. Brand, J. Chem. Phys. **80**, 3197 (1984).
11. A. Yokoyama, X. Zhao, E.J. Hintsa, R.E. Continetti, Y.T. Lee, J. Chem. Phys. **92**, 4222 (1990).
12. M.L. Yerram, J.D. Brenner, K.D. King, J.R. Barker, J. Phys. Chem. **94**, 6341 (1990).
13. D.H. Semmes, J.S. Baskin, A.H. Zewail, J. Chem. Phys. **92**, 3359 (1990).
14. J.C. Alfano, S.J. Martinez III, D. H. Levy, J. Chem. Phys. **91**, 7302 (1989).
15. R.M. Hochstrasser, D.A. Wiersma, Israel J. Chem. **10**, 517 (1972).
16. G. Castro, R.M. Hochstrasser, J. Chem. Phys. **46**, 3617 (1967).
17. J.A. Beswick, J. Jortner, J. Chem. Phys. **68**, 2277 (1978).
18. Y.S. Choi, C.B. Moore, J. Chem. Phys. **94**, 5414 (1991).
19. Y.S. Choi, C.B. Moore, J. Chem. Phys. **97**, 1010 (1992).
20. H. Hornburger, C.M. Sharp, M. Melzig, J. Phys. Chem. **95**, 8680 (1991).
21. H. Hornburger, C.M. Sharp, M. Melzig, Z. Phys. D: Atoms, Molecules and Clusters **25**, 67 (1992).
22. K.G. Spears, S.A. Rice, J. Chem. Phys. **55**, 5561 (1971).
23. E. Riedle, Th. Weber, U. Schubert, H.J. Neusser, E.W. Schlag, J. Chem. Phys. **93**, 967 (1990).

24. F. Metz, Chem. Phys. **9**, 121 (1975).
25. S.H. Lin, J. Chem. Phys. **44**, 3759 (1966).
26. H. Hornburger, C.M. Sharp, S. Leach, Chem. Phys. **101**, 67 (1986).
27. We have already investigated models where Morse-oscillator potentials for the ν_1 and a Rosen-Morse potential for the ν_4 vibration are assumed. At the moment it is still unclear why anharmonicities of these modes show so very small effects. Harmonic potentials seem therefore to be quite suitable approximations.
28. B.R. Henry, W. Siebrand, J. Chem. Phys. **49**, 5369 (1968).
29. A. Helman, R.A. Marcus, J. Chem. Phys. **99**, 5002, 5011 (1993).
30. B.A. Waite, W.H. Miller, J. Chem. Phys. **73**, 3713 (1980).
31. B.A. Waite, S.K. Gray, W.H. Miller, J. Chem. Phys. **78**, 259 (1983).
32. W.H. Miller, J. Am. Chem. Soc. **101**, 6810 (1979).
33. B.A. Waite, W.H. Miller, J. Chem. Phys. **76**, 2412 (1982).
34. V.S. Olkhovsky, E. Recami, Phys. Rep. **214**, 339 (1992).
35. A.A. Stuchebrukhov, R.A. Marcus, J. Chem. Phys. **98**, 8443 (1993).
36. M. Kleber, Phys. Rep. **236**, 331 (1994).
37. R.P. Feynman, F.L. Vernon, Jr., Ann. Phys. (N.Y.) **24**, 118 (1963).
38. A.J. Leggett, S. Chakravarty, A.T. Dorsey, M.P.A. Fisher, A. Garg, W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
39. H. Hornburger, M. Melzig, *et al.*, in preparation.
40. A.L. Sobolewsky, W. Domcke, Chem. Phys. **184**, 115 (1994).
41. Y. Yamaguchi, S.S. Wesolowski, T.J. Van Huis, H.F. Schaefer III, J. Chem. Phys. **108**, 5281 (1997).
42. T. Yamamoto, S. Kato, J. Chem. Phys. **107**, 6114 (1997).
43. I.J. Palmer, I.N. Ragazos, F. Bernardi, M. Olivucci, M.A. Robb, J. Am. Chem. Soc. **115**, 673 (1993).