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Rotational Effects on the Channel Three Decay in Benzene: in Support of the Preisomerization Mechanism[1)]

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The "Channel 3" phenomena in benzene were investigated concerning a model scheme as an extension of that applied for a typical intermediate case molecule, pyrazine. Using a multiple doorway-states formalism, the difficulties in interpreting such as insufficient density of states for the intermediate *dark* levels were eliminated based on a *pre*isomerization diagram involving a benzene isomer, most probably benzvalene. By a detailed examination of information about the title subject in the literature concerning both experiments and theory, several questions were raised and answered while making proposals for further study.

As a consequence of more than twenty years of research activities,[1—19)] at least one consensus has been reached concerning the Channel 3 mechanism in benzene: It is nothing but an extremely fast $S_1 \rightsquigarrow S_0$ **i**nternal **c**onversion (IC) through some intermediate (dark) states, as indicated by such data as broad absorption lines, low fluorescence quantum yields, and fast fluorescence decay rates. Among various experimental data, rotationally resolved information seems to be most useful. In spite of their *unexpected* observation (with the dependence on the rotational quantum numbers, J and K), they could remove various ambiguities for establishing a scheme.[7)] However, questions still remain for a more quantitative interpretation, e.g., how to rationalize the estimated density-of-states for the intermediate dark levels.[17)] Also, a dispute about the nature of the intermediate states, i.e., whether isomer levels are involved or not, has not yet settled. Furthermore, from my point of view, most papers appear to be written without any keen criticisms to the opponents (while examining their details). Take my case as an example: As early as in 1978, the present author proposed a simple, but realistic, mechanism in which the energy levels of isomer(s) are incorporated as intermediate states of the $S_1 \rightsquigarrow S_0$ IC.[3)] Unfortunately, this does not appear to be well taken judging from the way my paper was cited. (For example, I never insisted that benzvalene is formed after Channel 3 under isolated conditions.) This kind of misunderstanding may be one of the reasons for the far-reaching establishment of a consensus. Regarding this, few *comprehensive* review papers on the Channel 3 have been published so far, though many review papers have touched on this puzzle.

Recently, in a series of papers concerning rotational effects on radiationless transitions, Parts I—IV,[20)] the present author introduced a new kind of scheme for a typical intermediate-case molecule, pyrazine and its related molecule, pyrimidine, and their deuterium (D)-substituted compounds with successful results. The following gives its major ingredients: (1) Full utilization of the **m**olecular **s**ymmetry **g**roup (MSG) to describe rovibronic levels. (2) *Axis-switching* (in the widest meaning)[20—22)] in $S_1 \leftarrow S_0$ radiative transitions to allow for *intensity* mixing among rotational levels with a common symmetry (different in K; even without the perturbation for the mixing of states). (3) Multiple doorway-states formalism to assure above assertions. With the schemes and formalisms based on the above novel ideas, the difficulty (*enigma*)[23d)] to describe the rotational effects in the azines was mostly removed. By the way, the doorway-states concept had been little appreciated in *this* field of photophysics in spite of its success in the field of nuclear physics.[20,24,25)]

The purpose of the present paper is to apply the above outcome in the azines to resolve the difficulties which we may encounter in interpreting Channel 3 phenomena. Namely, this study is a natural development of the work by the present author in the two fields.[3,20)]

In Section 1, experimental data, as judged to be worthwhile by the author,[2,4,7,9,16)] are examined. Just like in my previous papers,[20)] I pick up only a restricted number of papers and experimental data. The criterion for choice is rather for my convenience and may partly be ascribed to the simplicity of the experimental data. By the way, the omitted information, which may be found in the cited references, is what can be interpreted with an "adequate" choice of parameters.

The important theoretical results that must be taken into consideration, from the author's point of view,[11—14,17,18)] are reviewed in Section 2. Here, again, clarity (e.g., more recent one) is honored more than priority.

A theoretical framework adequate for Channel 3 is presented in Section 3 by expanding that in a previous paper (Part II).[20b)] Since no quantitative application of the equations (evaluation of the formulas) is intended in this paper, only a brief summary is made in Section 3.1, while emphasizing the modifications. A detailed examination of the factors (parameters) required to apply the formalism to benzene is also made in the second part, which is followed by Section 3.3 for a discussion of the MSGs of benzene and benzvalene in a form that can suggest a correlation diagram for interconversion between them. These approaches just correspond to those adopted for radiationless transitions in azines.

In the core of Section 4, *case-by-case* discussions of the observations, as described in Section 1, are made by taking into account the theoretical work presented in Sections 2 & 3. This is preceded by an emphasis on the isomer, benzvalene, though the other isomers may not be completely disregarded (Section 4.1). The success of this interpretation may be considered in two ways: (1) A further emphasis on the capable multiple doorway-states formalism (without the *essential* help of axis-switching).[20] (2) Support for the *pre*isomerization mechanism in the Channel 3 of benzene, which had not been well taken.[3]

Finally, in the last Section 5 of Conclusion, a comment is made concerning the *view* of the simple $S_1 \rightsquigarrow S_0$ IC.[7,11] Further remarks are also made on various questions to be raised while investigating the Channel 3 phenomena. A proposal for new kinds of studies may be found as well.

1. Experimental Data Subject to Discussion

1.1. Rotationally-Resolved Spectral Data.[7] As mentioned in Introduction, the data in this section should be the most useful for discussing the Channel 3 mechanism.

1.1.1. Rotational Levels in the $14^1 1^2$ Vibrational State of Benzene.[7a,7b] By utilizing a two-photon excitation technique, Riedle and Neusser[7a] observed a highly-resolved spectrum of the $14^1_0 1^2_0$ band located at 3412 cm^{-1} above the 0,0 band under the Doppler-free condition. The obtained line widths of the J_0 levels (J_K levels with $K = 0$) for $J = 0$—14 are consistent with fluorescence lifetimes measured later by Schubert et al.[7b] belonging to the same group. Since the other transitions, i.e. those to the J_K ($K \neq 0$) levels, have not been detected (except for J_J, i.e. J_K with $K = J$ around $J \approx 35$ and a few unidentified levels), these levels can be regarded as being "forbidden" components for Channel 3. Of course, this prohibition is not perfect, as evidenced, e.g. in the relatively large differences (at about one order-of-magnitude) of widths and lifetimes between those in the $14^1_0 1^1_0$ and $14^1_0 1^2_0$ bands.[7a,7b]

The *foretoken* of the Channel 3 phenomenon described above was, by them, attributed to a Coriolis coupling of the concerned *light* level (the assigned zeroth-order level) to a *dark* level assessed to be broadened by the fast $S_1 \rightsquigarrow S_0$ IC.[7b] An observation of the J_0 levels seems to indicate the predominance of a parallel (z) Coriolis coupling. However, the appearance of the J_J levels supports a perpendicular (x, y) Coriolis coupling. These *apparently* mutually inconsistent judgments would force us to rely on their accidental deviation from close coupling with broadened levels whose locations are subtly dependent on the rotational quantum numbers (J and K) of the perturb*ed* levels. For the J_K levels with lower J (< 15), the nearby dark levels are only those that can be coupled by the parallel Coriolis coupling term. However, for the J_K levels with $J \approx 35$ (and $K \approx J$, near to the bottom of the group of rotational levels with a common J), those coupled by a perpendicular Coriolis coupling are located nearby. In other words, the other undetected rotational levels, e.g. those with J_K ($K \neq 0$, J) have at least one broadened level at a location close *enough* to couple. These may be called the "allowed" components, in contrast with the "forbidden" components. Hereafter, we use this terminology.

1.1.2. Rotational Levels in the $6^1 1^3$ Vibrational State of Benzene.[7c] Similar experiments as those mentioned above were performed by the same group for the $6^1_0 1^3_0$ one-photon band at 3287 cm^{-1} above the 0,0 band, i.e. slightly closer to the onset of Channel 3 than the above. Besides fluorescence detection, a delayed resonance-enhanced **multi**photon **i**onization (MPI) technique was used for a better resolution of the rotational structure. Here again, only a restricted number of rotational levels were detected. Against the case of the $14^1 1^2$ state, the dependence on the rotational quantum numbers (J and K) is not very systematic, though the lower K values are predominant. Therefore, they had to assume very intricate resonance and interference conditions. Namely, more than one dark state is thought to be involved in the Channel 3 mechanism around the $6^1 1^3$ vibrational state, where some accidentally "forbidden" components are evidenced. Rashev made a more detailed consideration on this data (Section 2.3).[17]

The intricate interplay of the rotational dependence of the coupling elements and accidental resonances which lead to interference of possible decay channels was further emphasized in a later (review) paper by the same group.[7d] This was done by putting together all of these experimental data on the rotationally selective disappearance of lines, including those in the $14^1_0 1^2_0$ band of $^{13}C_6H_6$, with the conclusion of its *less* significant dependence on the vibrational character and symmetry of the excited state *than* that on the excess energy.

1.2. Time- Domain Experiments with Picosecond Lasers.[9a,9c] Sumitani et al. made a picosecond fluorescence investigation on Channel 3 decay in benzene.[9a] Though they observed various transitions below and above the Channel 3 threshold, only the data on the $6^1_0 1^3_0$ band are examined here, corresponding to the preceding Subsection 1.1.2. The decay curve after excitation by a laser with a pulse width of $\tau_d \approx 10$ ps was so non-exponential that it could be reproduced by assuming two components with $\tau_1 = 0.25$ ns (weight 0.88) and $\tau_2 = 2.9$ ns (weight 0.12), respectively. This agreed well to the *rise* curve of the *hot* S_0 benzene observed by the same group.[9c] They interpreted this fluorescence decay by using a kinetic scheme involving the S_1 state and another non-fluorescent state, X, with a relatively long lifetime, that may be identified with an isomer (located ca. 2000 cm^{-1} *above* S_{10} in *their* Fig. 5).[9a] In opposition to this, however, the decay curve was also interpreted as being the effective average of the rotational levels, J and K.[7c] By the way, the kinetic scheme can be easily translated into its quantum-mechanical counterparts,[20,26,27] including that used by Riedle et al.[7] However, their estimated ratio $C_2/C_1 \approx 0.14$ (of the preexponential factors; not $\ll 1$) is not in conformity to the common situation of the intermediate case with a single doorway state.[20)] This is a subject for later discussion (Subsection 4.2.2).

1.3. Deuterium Isotope Effect.[6b,9b)] The deuterium (D) effect may be one of the important means to investigate the *protonated* species.[20d)] O'Connor et al.[9b)] observed the fluorescence decay of C_6D_6 with an identical apparatus and procedures to those used for C_6H_6.[9a)] Two kinds of differences in the Channel 3 region should be pointed out: (1) Broader bands in both the absorption and fluorescence excitation spectra of C_6D_6 compared to those of C_6H_6. (2) Purely exponential decay in C_6D_6, in contrast to the non-exponential decay in C_6H_6. These appear just like a manifestation of the statistical-limit behavior in C_6D_6 against the near intermediate-case behavior in C_6H_6 that is ascribed to the higher density of states in C_6D_6 than in C_6H_6 around the Channel 3 region.[20,26,27)] Similar D effects are noted for pyrazines.[20d)] Although the $S_1 \rightsquigarrow S_0$ IC of benzene is well established to be in the statistical limit, even for the S_{10} level, i.e. the ground vibrational level of the S_1 state, this is not always the case for the $S_1 \rightsquigarrow X \rightsquigarrow S_0$ process involving the sparse intermediate state X.[20,26,27)]

1.4. Miscellaneous.[2c,4b,16)] In the above sections, what may be taken to be important by most people are discussed. In this section, a collection of experimental data that drew the author's own attention is presented, other than those described above.

1.4.1. Photochemistry of Benzene Isomers.[4b)] Harman et al. studied the photochemistry in two valence isomers of benzene, i.e. benzvalene and Dewar benzene, detecting clean isomerization towards benzene with high quantum yields. From a symmetry consideration, they concluded that isomerization occurs in an orbitally forbidden (with the orbital part of the purely electronic matrix element being canceled), but spin-allowed, process, such as that by a vibronic mechanism. The same would apply for the contrary processes, i.e. interconversions of $^1B_{2u}$ benzene to the ground states of the isomers that may be related to Channel 3 of benzene.

1.4.2. Isotopically Scrambled Photoproducts of 1,3,5-Trideuteriobenzene.[2c)] Callomon and Somers tested possible roles of valence isomers as intermediates in the unimolecular non-radiative relaxation of the S_1 state of benzene, including the fast Channel 3 process, by irradiating the 260 nm absorption system of 1,3,5-trideuteriobenzene, in the vapor phase. No evidence was found for the involvement of the (transient) valence isomers, such as prefulvene, with little isotopically scrambled products.[2c)] However, this will be critically examined in view of MSG (Subsection 4.1.2).

1.4.3. Non-Fluorescent Transient Species.[16)] As described in Section 1.2, the observed non-exponential decay[9a)] and rise[9c)] were interpreted as evidence of the non-fluorescent state, X, though this was a subject for criticism.[7c)] By utilizing (delayed) **r**esonance-**e**nhanced two-**p**hoton **i**onization (RE2PI) **t**ime-**o**f-**f**light (TOF) mass spectrometry, Ichimura et al.[16)] detected a transient species with a lifetime of 3.5 ns (for the $6^1 1^3$ level case), which almost corresponds to the τ_2 (ca. 2.9 ns) component of the fluorescence (Section 1.2). However, its contribution of 0.29—0.67 was larger than that (0.12) of the τ_2 component. Somehow, this was taken as being additional evidence of the non-fluorescent transient species, against the theory of the direct $S_1 \rightsquigarrow S_0$ IC (Section 2.1).[11)] This is also the subject for a later examination (Subsection 4.2.2).

2. Theoretical Results to Be Taken into Account

As discussed in the preceding Section, and will be discussed later, the dispute concerning the nature of the intermediate state in Channel 3, i.e. whether isomers are involved or not, cannot be settled by the experimental data alone. Therefore, the theoretical data to support the *both* schemes will be examined.

2.1. Calculation of the Rates of Pure $S_1 \rightsquigarrow S_0$ IC.[11)] A calculation *of* the excess energy dependence of the rates of radiationless transitions and *of* its D effect is one of the important means to clarify their mechanisms, in spite of the difficulty to reproduce the absolute experimental decay rates. In a series of papers, Hornburger et al. did this for the $S_1 \rightsquigarrow S_0$ IC of benzene, with results in fairly good correspondences to the experimental data. The most significant outcome may be the larger contribution of the b_{2g} type out-of-plane skeletal ν_4 vibration at higher excess energies. Thus, they suggested *no need* to assume a contribution of the isomer levels for Channel 3.

2.2. Theoretical Calculation of Potential Energy Surfaces.[12—14a)] By such as the MCSCF-CI method on the MIDI4 basis, Kato calculated the (16-dimensional) potential-energy surfaces of benzene *around* the reaction path for the (S_1) benzene-prefulvene interconversion retaining C_s symmetry (the disrotatory path), and found a crossing point (surface) between S_1 and S_0.[12)] Thus, the observed steep rise of the decay rates above the crossing point could be interpreted by a surface-hopping transition through a tunneling mechanism.

A more detailed calculation was performed in a recent paper by Sobolewski et al.[13)] using complete-active-space SCF *and* multireference CI techniques, that appeared near the end of this work. The conical intersection of the lowest $\pi\pi^*$ excited singlet surface with the S_0 surface was mapped out in *two* dimensions: the reaction coordinate to prefulvene of a$'$ symmetry for the C_s point group *and* the coordinate of maximum coupling of a$''$ symmetry perpendicular to it. Thus, an ultra-fast internal conversion through the funnel is naturally introduced.[13)] However, with only these double-layered potential surfaces, little description can be made of the phenomena *after* passing through the funnel. By the way, this calculation is in conformity to speculation (predictive discussion) by the present author (Subsection 4.1.1).[1a,3)]

In a more recent paper by Palmer et al.,[14a)] potential surfaces extending to the region of C_1 symmetry, including the area of the isomer, benzvalene (of C_{2v} symmetry), were actually obtained on an MC-SCF/4-31G basis. The following gives the major conclusions concerning the reaction path:

(1) The ground-state potential-energy surface along the reaction path between benzene and benzvalene has a flat diradicaloid region (named as "prebenzvalene") correspond-

ing to prefulvene. However, prefulvene, itself, is a transition state.

(2) The S_1 reaction path from benzene toward prefulvene contains an excited-state minimum with D_{6h} symmetry *and* a transition state between this minimum and a prefulvene diradicaloid located on the ground-state surface. A cone is found between the transition state and prefulvene.

Thus, as summarized in their Scheme II, the computed S_1 reaction path involves passage over the transition state, followed by a return to the ground state via a fully efficient decay through the conical intersection region near to "prebenzvalene". By the way, it should not be overlooked that Channel 3 is the radiationless transition in the isolated condition, i.e. with conservation of energy high enough to distribute even over the area of unstable prefulvene. In conclusion, this calculation is more close to my conjecture just mentioned above (Subsection 4.1.1).[1,3]

2.3. An Analysis of the Interaction Mechanism for the Rotational Levels in the $6^1 1^3$ State of Benzene.[17] Rashev carried out a detailed analysis of the data described in Subsection 1.1.2. First of all, in this case, an anharmonic coupling term is shown to be predominant over the *z* Coriolis coupling term by means of a numerical analysis and group-theoretical consideration. (Though the *perpendicular* Coriolis coupling may have any contribution in a form different from that of anharmonic coupling, there is no experimental evidence to support this possibility). Therefore, the observed dependence on the rotational quantum numbers has to be interpreted based on the fortuities in the distributions *of* the locations of the energy levels and *of* their coupling matrix elements, mostly by anharmonic terms, reinforcing the arguments given in Section 1.1(.2). However, difficulties remain in interpreting the density of states for the intermediate *dark* levels reduced from the experimental data: The density of vibrational levels ρ_v calculated by using available spectroscopical data (of course, below the Channel 3) is *at least* one order-of-magnitude less than that required.

2.4. Calculation of the Rotational Lines in the Fluorescence Excitation Spectra of the $14^1 1^2$ band of S_1 Benzene.[18] In a more recent paper,[18b] which drew my attention after submission of the initial version of this paper, Helman and Marcus calculated the excitation spectra for various J and K under several assumptions, and succeeded in reproducing the observed spectra (of the forbidden component, at least; Subsection 1.1.1). Their assumptions and conclusions may be classified as follows:

(1) The transition is assumed to be a (pure) internal conversion from an *single* quasi molecular eigenstate in S_1 to a set of molecular eigenstates in S_0. Furthermore,

(2) no nearby dark state is assumed, even off-resonantly, while the contribution of various dark levels is taken into account only in a perturbing expansion. These assumptions are apparently beyond the scope of what is discussed in Subsection 1.1.1, where an explicit contribution of the dark state is assumed.

(3) For both initial and final states, a perturbation expansion is applied on the basis of **r**igid-**r**otor **h**armonic-**o**scillator (RRHO) states. These states may be taken to correspond to the **d**iabatic **B**orn–**O**ppenheimer (DBO) basis that takes account of *neither* the isomer levels *nor* the anharmonicity towards isomerization, as described later (Section 3.1).

All of these assessments may be adequate, at least for the forbidden component. Furthermore, the success of this calculation should be regarded as supporting evidence for assumption (2) of *no* nearby dark level for the forbidden component, as just described above. However, their calculation also *predicted* some lines (e.g., J_K lines with $K = 1$ or 2 (besides $K = 0$) for lower J) that are not evident in the observed excitation spectra. Therefore, the outcome of this calculation should also be considered as additional evidence of the dark state that is prerequisite for the allowed component, though the authors themselves did not noted this.

3. Theory

As introduced, this Section is divided into three sections, the first two of which match Sections 3 & 4 of "Part II".[20b] Namely, the first one is devoted to expanding the Theoretical Framework developed for pyrazine and its related molecules[20] to apply for the present system, i.e. benzene in the Channel 3 region. The second is for drawing more realistic pictures of what is actually happening. Finally, a discussion of the MSGs of the two species, i.e. benzene and benzvalene, is made as may be related to the *possible* "correlation diagram" (about correspondent to the combination of Fig. 1 of Ref. 3 and Fig. 3 of Ref. 4b).

3.1. Formalism. The whole scheme that the author believes to be most adequate is presented from the beginning, without mentioning any other possible alternatives. Support for this theory can be found in the successful interpretation of the experimental facts to be made in Section 4. Instead of *r*ederiving Eqs. 1—30 by modifying those in Part II, only those portions to be modified are emphasized. For that purpose, to sketch an illustration, i.e. to show a modified version of Fig. 1 in Part II (as the simplest symbolical expression) may be most suitable. From Fig. 1 of *this* paper, two dissipative continua, i.e. **r**adiative $\{r\}$ *and* non-radiative $\{c\}$ **c**ontinua to be drawn at the left *and* at right sides, respectively, are omitted in order to emphasize the difference and to avoid any complex appearance of the figure. In short, the states, $\{r\}$, s_0, $\{s\}$ with discrete N_s ($=2$, in this figure) members, $\{i\}$ with N_i ($=4$, in the figure) members, and $\{c\}$ represent the zeroth-order states assumed to be adequate for describing the dynamics in benzene: $|r>$ for the system composed of a molecule in a (lower) rovibrational level of the ground state *and* a photon, $|s_0>$ and $|s>$ for fluorescent levels, $|i>$ for an **i**somer level, and $|c>$ for a higher rovibrational level in the ground state, respectively (vide infra). (For details concerning the scheme as represented by this figure, the reader is encouraged to consult Ref. 20b.) However, in contrast to the case of azines, the zeroth-order states are not the eigenstates of the conventional Hamiltonian (e.g. Eqs. 6 in Part II). Rather, for them (except for $\{r\}$), a more crude Hamiltonian should be imagined to correspond to the *real* zeroth-order states (wavepackets, as illustrated in Fig. 1 of Ref. 3). The strongest evidence for this assessment may be traced to the actual existence of benzvalene as a chemical identity with a heat of formation well below the S_1 benzene.[4,14] Comments on the possible alternative isomers for $\{i\}$ will be given later (Section 5). Namely, *new* zeroth-order and perturbing (residual) Hamiltonian*s* are defined as follows:

$$H_0 = H^{(e)}_{\mathrm{e,PSDBO}} - H^{e}_{\mathrm{anh}} + H^{e}_{\mathrm{v}} + H^{e}_{\mathrm{r}} + H^{(e)}_{\mathrm{S}} + H^{(e)}_{\mathrm{I}}, \tag{1a}$$

$$V = H^{e}_{\mathrm{ev}} + H^{e}_{\mathrm{anh}} + H^{(e)}_{\mathrm{nBO}} + H_{\mathrm{SO}} + H^{e}_{\mathrm{vr}} + H^{(e)}_{\mathrm{rS}} + H^{(e)}_{\mathrm{SI}}. \tag{1b}$$

The most significant differences of these equations from the previous Eqs. 6 in Part II are in the first terms of the both equations: For the first Eq. 1a, the subscript PSDBO against PSABO for **p**ure-**s**pin **a**diabatic **B**orn–**O**ppenheimer (approximation). The DBO (**d**iabatic B–O) basis set formed by eigenfunctions of H_0 in the *present* DBO approximation is believed to be suitable for describing either the nearly degenerate electronic states or those involved in chemical reactions with level crossings.[3,26] Therefore, the first term in the second Eq. 1b, i.e. the H_{ev} (vibronic; the superscript e to indicate electronic-state dependency is abbreviated hereafter) term works to couple the rovibrational levels of different electronic states at the extent beyond the **H**erzberg–**T**eller (HT) expansion (so as to pass through the barrier).[26] The anharmonic term, H_{anh}, is nearly equivalent to H_{ivr} in the previous equations, but does not always give rise to an **i**ntramolecular **v**ibrational energy **r**edistribution (IVR) (vide infra).[20,26] For example, the major anharmonic terms evident in the vibrational structure, including Fermi resonances, such as cubic terms, are *already* contained in $H_{\mathrm{e,PSDBO}}$. (The harmonic approximation is a too crude approximation to be used in the field *of* molecular spectroscopy, and, accordingly, *of* molecular photophysics.) As in Part II, $|r> = |\mathbf{g}, \boldsymbol{k}, \boldsymbol{e}>$ represents a system composed *of* a molecule (benzene) in a lower rovibronic level, $\mathbf{g} = (g, v, r)$ belonging to the **g**round electronic state, $g = \mathrm{S}_0$ and *of* a photon denoted by $(\boldsymbol{k}, \boldsymbol{e})$. The initial state $|r_0> = |g_0, k_0, e_0>$ belongs to this group $\{r\}$. However, $|s_0>$ represents a molecule (plus a vacuum electromagnetic field) in a state (within the S_1 state) directly coupled to $|r_0>$ radiatively, i.e. in a spectroscopically assigned level. Its nearby states within the S_1 state, as represented by $\{s\}$, are possibly coupled to the s_0 state with the H_{anh} (other than those *already* included) and/or H_{vr} (**v**ibration-**r**otation interaction Hamiltonian, including H_{Cor} for **Cor**iolis coupling) term. Though $\{s\}$ are not coupled to r_0, their coupling among themselves and with various $\{r\}$ states is not forbidden. If the number of $\{s\}$ states, i.e. N_{s}, is big enough, s_0–$\{s\}$ coupling *may* then cause a radiationless transition, called IVR.[26] Actually this is not the case, however, with $N_{\mathrm{s}} < 10$,[20] against the $\{t\}$ states in pyrazines where *complete scrambling* by H_{vr} could be assumed, probably with the predominant help of H_{SO} *and* H_{SI} (H_{hfs}) for spin-orbit and **h**yperfine interactions.[20] The $\{s\}$ states are subsequently coupled to $\{i\}$ states, i.e. rovibrational levels on the DBO potential of the **i**somer, benzvalene by H_{ev}. A similar coupling scheme exists between $\{i\}$ and $\{c\}$. If the sequential decay $\{s\}\rightarrow\{i\}\rightarrow\{c\}$ is to be observed, it may be called as "*pre*isomerization", regardless of whether the isomer is detected or not.[1a,3] The above formalism (under the assumption of the isomer) is a complete one, in view of the complementarity principle of quantum mechanics (independent of the choice of basis set).[26] However, for more detailed descriptions, we may have to rely on other basis sets, like rovibrational levels on the ABO potential (for faster convergence),[26] as will be done later.

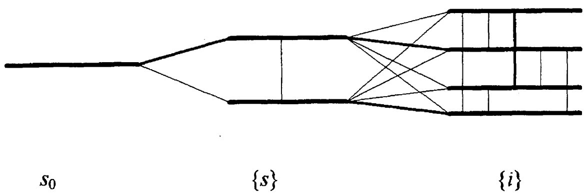

Fig. 1. An energy level scheme for the doorway-states formalism concerning the rotational effect on the Channel 3 mechanism in benzene. The difference in the thickness of the lines, connecting the levels, is to hint the variation of the coupling strengths.

Now that a modification of the scheme is made to apply for the present system, the next thing to do is to derive the corresponding modified equations. At first sight, a direct application seems to be difficult, since one more step is added in the new scheme. However, a close examination of the derivation reveals that the formalism is not dependent on the number of steps (i.e., on the choice of basis sets in conformity to the complementarity principle of quantum mechanics). Actually, prediagonalization within the set of s_0 and $\{s\}$ shown in the *new* Fig. 1 immediately reduces it to the *old* Fig. 1 (of Part II).[20b] Therefore, the importance of the doorway-states description is again emphasized, though the role of axis-switching is now taken over by the actual coupling, H_{anh} or H_{vr}. Since we do not intend to evaluate the equations, no more talk is necessary, except for pointing out that the *forms* of Eqs. 19 *and* 29 as principal concluding equations in Part II, are not modified at all. The *first* Eq. 19 contains the interference effect in multiple transitions connected with various doorway states, i.e. manifesting IVR in this case. The *second* Eqs. 29 contain *interfering* contributions from the *independently decaying levels* as eigenfunctions of an **eff**ective hamiltonian, $\mathsf{H}_{\mathrm{eff}}$ (similar to Eq. 21 in Section 3.6 of Part II) manifesting non-exponential (multiple exponential) decay. A detailed examination of the experimental data using the schemes will be made in Section 4 in forms dependent on the experimental details.

3.2. Description of the Channel 3 Phenomena. The first thing to do is to identify the molecular doorway state, N_0, as a superposition of all of the excited states weighted by its strength of radiative coupling with the initial ground state, g_0 (as defined by Eqs. 15 of Part II). In the present case, it is nothing but the zeroth-order state, s_0, as defined in the above section and shown in Fig. 1. Against the case of azines, where axis-switching is a primary cause of depolarization,[20] the doorway states used to describe the present case are composed of s_0 and $\{s\}$, all with different shapes (vibrational structures) of fluorescence spectra to be *able to exhibit* IVR. In any case, the decay process after ps laser excitation can be interpreted as a sequential decay that consists of the IVR and subsequent two-step isomerizations, at least formally.[3)] However, all of the steps (i.e. zero order states) may not be well distinguished from one another, depending on the magnitudes of the coupling matrix elements $\{v_{ij}\}$ and the energy separations $\{\Delta E_{ij}\}$ with $\{i{\neq}j\} = \{s_0, \{s\}, \{i\}, \{c\}\}$, and of course, *on* the densities of states to establish the number of coupled states, N_s and N_i, and the total number, i.e. their sum, N_s+N_i+1. Since $\{c\}$ are almost continuous, the parameters involving them, including N_c, should be *used* only for a model representation of the real event.[20,26,27)] The observed fast and slow decay components[9)] may be ascribed to the fastest and slowest steps of the decay (including dephasing) process, respectively, just like in kinetics, whose identifications are made in the next Section 4.[20,26,27)]

The next necessary thing to do is to describe the *resonance* (quasieigenstate), as observed in the high resolution spectra.[7)] Their data remind us of similar data for the azines by Meerts et al. including spectra composed of those for transitions into *bunches* of **m**olecular **e**igen**s**tates (MESs) observed in pyrazine for lower J (= 0—4).[23)] Here, in benzene, a Lorentzian takes over the bunch (in pyrazine) with a width orders-of-magnitude larger than that of the MES in the latter. The MES of the azine is a mixture of $\{s\}$ and $\{t\}$ where triplet components are predominant.[20)] In the present case, the resonance may be *either* the rovibronic level in the S_1 state under the DBO approximation (after $H_{\rm anh}$ or $H_{\rm vr}$, i.e. a mixture of s_0 and $\{s\}$) *or* that on the ABO potential surface around the S_1 benzene (after $H_{\rm ev}$ *too*, partially extending to the *g* state of benzvalene, i.e. that of s_0, $\{s\}$, and $\{i\}$), to be represented as the eigenfunction of the effective hamiltonian $\mathsf{H}_{\rm eff}$ (preceding Section 3.1). Considering high-density of states corresponding to the excess energy of ca. 20000 cm^{-1},[4b)] a full extension towards benzvalene, i.e. full inclusion of $\{i\}$ states, should be disregarded. In other words, the resonances cannot be simply described as eigenstates (to be named as MESs) of another effective Hamiltonian on the *full* $s_0+\{s\}+\{i\}$ basis, that may be represented as $\hat{H}^0_{\rm m}$ (in correspondence to Eq. 30 in Section 3.7 of Ref. 20b). This Hamiltonian was originally introduced to apply for the azine on the $\{s\}+\{t\}$ basis. (Even complete scrambling could be assumed for pyrazines, due to $H_{\rm SO}$, $H_{\rm vr}$, and even $H_{\rm hfs}$.[20)]) To say more strictly, the majority of $\{i\}$ with n_i members ($N_i-n_i < n_i$; on the DBO basis that might be *either* out of coupling with $\{s\}$ *or* strongly coupled to $\{c\}$) has to be excluded. Actually, only a few (0—2 ?) resonances are identified for each observed band (s_0),[7)] though the number of resonances, n_s, could be as many as $N_s+N_i-n_i+1$. Contrary to this, the $N_s+N_i-n_s-n_i+1$ *hidden resonances* (not detected *yet* ?) might be distributed over the whole ABO potential surface (Subsection 4.2.2).

Finally, possible reasons for the *too high* density of states (Section 2.3) are enlisted: (1) N_i in addition to N_s. (2) Rovibronic levels on the ABO potential just described above. These are our presumptions. More detailed specific discussions will be made in the next Section 4. Especially, support for the latter, i.e. (2) will be found in Subsection 4.2.2.

3.3. MSG of Benzene and Benzvalene. Group theory demands that the rotating non-rigid molecule is described by the MSG.[21)] Namely, its wavefunctions *can* always be made to belong to the symmetry representation of MSG. This is the reason why we need this section. Since many review papers are available on the (point-) group theoretical discussion of these molecules,[4,5,21,28,29)] only what are to be adopted in the following discussion are described here.

3.3.1. MSG of Benzene. With a combination of Refs. 5 and 20, little is to be discussed here except for pointing out that benzene belongs to D_{6h}(M) MSG. Another important fact is that it is an oblate type symmetric top whose rotational level is described by two rotational quantum numbers, J & k with rotational constants, A ($=B$) & C ($=A/2$). Concerning the rotational effect, **n**uclear and **r**otational symmetry numbers, $\sigma_{\rm n} = \sigma_{\rm r} = 6$ should also be mentioned that is contained in the formula of the effective density of states for higher J with the rotational factor, $(2J+1)/\sigma$.[20d)]

3.3.2. MSG of Benzvalene. Benzvalene belongs to C_{2v}(M) MSG and is an asymmetric top with the label $J_{K_aK_c}$ for the rotational level. This applies *unless* this molecule is excited into a higher vibrational level where a description based on large-amplitude vibrations would be required.[18)] Benzvalene in the Channel 3 region *does* have the large excess energy. Therefore, we must use wavefunctions belonging to D_{6h}(M) instead of C_{2v}(M) (Subsection 4.1.2).

3.3.3. Correlation Diagram between Benzene and Benzvalene and Selection Rules for Their Interconversion. These species are different from each other in *both* symmetries *and* directions of the principal symmetry axes (z's; not of rotation). Therefore, little group-theoretical restriction is imposed upon the coupling between their rovibronic levels, as illustrated in Fig. 1 of Ref. 3, unless we are to discuss the actual (absolute) value of the matrix element, e.g. to see whether it is orbitally forbidden (Subsections 1.4.1 and 1.4.2)). Thus, the *only* group theoretical restriction is between their rotational levels with $\Delta J = 0$ and with little on K, due to axis-switching (including axis-interchange).[20—22)] Therefore, we don't need to cite the correlation diagram.[4,29)]

4. Discussion

This section is devoted to interpret the experimental data described in Section 1 based on the theory developed in the last Section. Therefore, what has to be confirmed is the adequacy of this theory, including several assumptions on which the former is based.

4.1. Support for an Isomer, Benzvalene. No direct evidence of the involvement of the isomer including benzvalene is given in the literature. However, there is much indirect experimental evidence,[4,29)] as already mentioned.[1,3)] Recent theoretical calculations of potential curves[12—14)] also appear to be consistent with this assessment. Most significantly, it could successfully interpret the experimental facts, while no evidence is indicated in the published papers to *disprove* the isomer. A few observations concerning this dispute are given below.

4.1.1. A Schematic Diagram with Level Crossings.[3,12—14] As *implied* in the first paragraph of Section 3, the location of the benzvalene g state in between the S_0 and S_1 states of benzene could be taken as the strongest evidence of the schematic diagram as of Fig. 1 in Ref. 3. (The Scheme II in Ref. 14a may be regarded as its improved version, with more refined details; vide infra.) With a detailed inspection of the potential surfaces of the S_1 benzene and the S_0 benzvalene by taking account of the spectroscopical data on molecular vibrations,[2a,4,5,28,29] the author has located a saddle point for their interconversion just below the "*unstable* ground state" of prefulvene that may exist near to a cone in multidimensional potential surface (Section 5).[1a]

Accordingly, the recently calculated potential curves (surfaces) of benzene are worth examining.[12—14] Actually, they appear to reinforce the above assumption. Since the crossing point between the S_1 benzene (extending to the *virtual* S_0 prefulvene) and the S_0 benzene is located under the restriction of C_s symmetry, a simple application of the Jahn–Teller effect[21] would predict saddle points at lower energy that could be continuous to the potential energy surfaces of the g state of benzvalene. In actuality, their calculations found the avoided crossing or the cone for the a″ displacement, depending on the scale of the computation.[12—14] This statement is equivalent to saying that prefulvene is not an intermediate state for the S_1 to benzvalene interconversion, though it might be a transient species in the condensed phase, e.g. for the S_2 to fulvene reaction.[3,29] Actually, the most recent calculation by Palmer et al.[14a] (with their Scheme II, while finding a shallow minimum of "prebenzvalene") is just in conformity to this speculation.

4.1.2. Interconversions Retaining D_{6h}(M) Symmetry. Now that the diagram is established, we can go ahead to make a more detailed discussion while appealing to the *classical* concepts in the field of radiationless transitions, such as promoting and accepting modes and densities of states.[26] Just like the case in azines,[20] MSG plays an important role in benzene that belongs to D_{6h}(M). Suppose that a molecule is excited into the lowest rotational (0_0) level in the $6^1 1^3$ state of S_1. It must belong to an irreducible representation, $B_{2u} \times e_{2g} \times a_{1g} = E_{1u}$ of the D_{6h}(M) MSG. Without colliding to another molecule, the system has to retain its symmetry property in the most period of the Channel 3 decay process. (Exception may be at the final step of the decay after excitation into the "forbidden" component with the long fluorescence lifetime.) Therefore, severe restrictions must be placed upon the couplings. A discussion of this kind was actually done on H_{anh} and H_{vr} couplings for the case of the $6^1 1^3$ level based on the **m**olecular **p**oint **g**roup (MPG).[17] Here, its effect on the *effective* density of states is examined. As to the S_1 benzene, no practical difference is seen in the descriptions between MPG and MSG, at the zeroth order. However, this is not the case for the other *species*. Certainly, D_{6h}(M)-type vibronic wavefunctions representing the *hot* (highly vibrationally excited) benzvalene can be approximately represented by linear combinations of vibronic wavefunctions belonging to *that* with a point group of C_{2v}.[21] Then, due to the enormous difference in the geometry that allows for significant scrambling, most of the formal selection rule may be reduced to that of only MSG, e.g., $\Delta J = 0$ only for the set of rotational angular momentum quantum numbers, due to strong effect of the *axis-switching* (on the *non*-radiative transition) equivalent to that of H_{vr} (Subsection 4.2.1).[20] However, in actuality, not all the level is accessible from the initial state due to the lack of efficient promoting and accepting modes, here again by the enormous geometry change.[26] Therefore, the effective density of states for the final states may not be as large as that predicted for *benzvalene* in the Channel 3 region with an excess energy of ca. 20000 cm^{-1} (Section 3.2); for vibrational wavefunctions of the *efficient* final states have to be distributed near the saddle point. One of the most effective coupling modes between the S_1 and the isomer may be that with vibrational angular momentum, e.g., l_{10} (l_{16}) mode originated from an e_{1g} (e_{2u}) type out-of-plane ν_{10} (ν_{16}) vibrations (for benzene),[1a—3,5] though the other modes of out-of-plane vibrations such as b_{2g} type ν_4 mode may be important as well. Imagine a potential energy surface (torus) containing 6 minima of benzvalene*s* (belonging to the C_{2v} MPG). These species over the minima would convert to one another, possibly through a combination of vibrational coordinates of the modes, such as $l_{10} + l_{16}$ (for benzene) over 6 barriers, whose saddle points are located near to the *feet* of prefulvene*s* (with shallow minima of prebenzvalene*s*[14a] ?).[1a] A similar argument would be applied to the case of the interconversion from benzvalene (prebenzvalene) to S_0 benzene.

The experiment on the possible isotopically scrambled photoproducts of 1,3,5-trideuteriobenzene with a *negative* result might have been taken to show no involvement of an isomer, like benzvalene.[2c] However, this can also be interpreted if we assume the retention of D_{3h}(M) symmetry during the sequential decay (Section 3.3). Imagine a 1,2,4-trideuteriobenzene molecule after being *relaxed* into the S_0 state, (i.e., over the S_0 potential minima of C_s symmetry of MPG) belonging to one of the irreducible representation of the D_{3h}(M) MSG, instead of C_s(M). It must be in a highly excited vibrational state with many quanta of the out-of-plane vibrations to retain the higher symmetry of D_{3h}(M). Therefore, its vibrational density of states must be much smaller than that of 1,3,5-trideuteriobenzene (of D_{3h} MPG) with the same excess energy. Furthermore, its C–H stretching vibrations can be good accepting modes for the interconversion (to the g state of the 1,3,5-substitute). Thus, the Franck–Condon weighted density of states[26] would be much larger for the 1,3,5-substitute than the 1,2,4-substitute. Indirect evidence of the *apparent* severe restriction on the s_0–$\{s\}$–$\{i\}$ coupling, as revealed below (Subsection 4.2.2), that might work for the partial survival of the scheme s_0–$\{s\}$–$\{c\}$ may also be interpreted by MSG in addition to the lack of efficient modes.

4.2. Interpretation of the *Selected* Experimental Data.[7,9] It is still necessary to interpret the experimental facts, as reviewed in Section 1. This has to be done based on the theoretical framework, as presented in Section

3, with full utilization of the knowledge developed above, including that in Section 2. Only a portion of them are selected, by omitting rather obvious points, as indicated in a few subsections of Section 2.

4.2.1. Rotationally-Resolved Spectral Data.[7)] As described in Sections 1.1, 2.3, and 3.2, the two sets of data only suggest complexities in the coupling between light and dark zeroth-order states with randomly distributed $\{v_{ij}\}$ and $\{\Delta E_{ij}\}$ values with $\{i{\neq}j\} = \{s_0, \{s\}, \{i\}\}$, depending on the properties and locations of the vibrational levels, as *illustrated* in Fig. 1. It is still necessary to determine whether the resonance is within S_1 or extended towards the benzvalene area (Section 3.2). In the case of the $6^1 1^3$ state, two facts are noted: (1) Insufficient density of states (of the zeroth order), at more than one order-of-magnitude (Section 2.3). (2) Evidence of non-fluorescent transient species (Sections 1.2 and 1.4.3). These can easily be interpreted if we assume the coupling between $\{s\}$ and $\{i\}$ beyond DBO approximation, at least partially (Section 3; with possible assistance of the axis-switching). Thus, the dark state may be identified as rovibronic levels on the ABO potential surface *either* around the S_1 benzene *or* extended towards benzvalene (or prebenzvalene). With little evidence of a higher density of states than that of the $6^1 1^3$ state (of e_{2g} symmetry), the same is expected for the $14^1 1^2$ state (of b_{2u} symmetry) located only 125 cm^{-1} above the former. Actually, the larger number ($4{\times}2$) of the available e_{2g} modes than that ($2{\times}1$) of the b_{2u} or a_{1g} modes would suggest rather the opposite case,[2a,5,17)] as appears to be consistent with the observation.[7c)]

One remark may be made on the conceivable alternative to $H_{\rm vr}$ ($H_{\rm Cor}$): The significant axis-switching between S_1 (s_0; The $\{s\}$ states are not always required to be involved.) and the isomer ($\{i\}$) *can* predict the same selectivity, letting the effective density of the final states (belonging to the **i**somer) be $^{J}\rho_{\rm I} = ((2J+1)/\sigma)\rho^{\rm i}_{\rm v}$ (for larger J) with the vibrational density of state $\rho^{\rm i}_{\rm v}$ and the symmetry number $\sigma = \sigma_{\rm n} = 6$ under the assumption of D_{6h}(M) symmetry (Subsection 4.1.2).[20d)]

4.2.2. The Non-Exponential Decay.[9,16)] If the theory in Section 3 is applied, the observed short (fluorescence) decay component should be interpreted as an average of those in the incoherent decays of various doorway s_0 states, i.e. with various J_0 and K_0, including those observed in high resolution spectra.[20)] If $\{c\}$ is not explicitly taken into account assuming a slow virtual (zeroth order) $\{i\}{\rightarrow}\{c\}$ decay, as *had* been done for a $\{t\}{\rightarrow}\{c\}$ decay in pyrazine, the doorway state, s_0, is shown to decay biexponentially with the ratio of preexponential factors $(N_{\rm s}+1)/N_{\rm i}$ (<1).[20)] Provided that this is applied for the $6^1 1^3$ state with the intensity ratio, $C_2/C_1 = 0.14$,[9a)] $N_{\rm i} \approx 7(N_{\rm s}+1)$ is derived, indicating *apparent* severe selectivity for the s_0–$\{s\}$–$\{i\}$ coupling in addition to such as those of MSG and $\Delta J = 0$ (Subsection 4.1.2). Namely, the coefficient of ca. 7 (not $\gg 1$) is definitely against the premise for the scheme of the intermediate case as *symbolically* represented by the Fig. 1.[20)] Therefore, a large number $(N_{\rm s}+N_{\rm i}-n_{\rm s}-n_{\rm i}+1)$ of *hidden* resonances not detected by fluorescence measurement have to be assumed for consistency, requiring an explicit involvement of $\{i\}$ *for* smaller quantum yields, i.e. *for* faster decay than the direct $S_1{\rightsquigarrow}S_0$ IC (Section 3.2). By the way, actual evaluation of the formula to reproduce the decay is not so straightforward; the intensity ratio between the τ_1 and τ_2 components seems to be strongly dependent on the rotational levels. For example, it is almost certain that the relative contribution of the forbidden components to the intensity of the long-lived component is larger than that of the allowed component. However, in order to interpret the whole intensity of the long-lived component by the contribution of the observed bands in high-resolution spectra, the weight (0.12) on the τ_2 component (for the $6^1 1^3$ case), i.e. the relative value of C_2 appears to be a little too big with more than 5-times the ratio *between* the number of observed transitions (*bright* resonances, Fig. 5 of Ref. 7c) *and* that of possible transitions (s_0) at room temperature: With a rotational constant, $B' = 0.18\ \mathrm{cm}^{-1}$, i.e. with $\langle J\rangle \approx 40$ from $\langle E(J,\ k)\rangle_k/B' = (5/6)J(J+1){\sim}2(\ln 2)(200/0.18){\sim}1500$, the ratio is estimated to be ca. $150/(40{\times}80{\times}2){\sim}0.02$.[2a,7c,17)] Therefore, most of the τ_2 component of less than 0.10 (ca. 0.12—0.02) to 0.12 (subject to the uncertainty due to ambiguities while *determining* individual parameters in kinetics[9a)]) has to be ascribed to the X state with lifetimes longer than average, even after excitation into the allowed components (as appears to be consistent with the observation: Subsection 1.4.3[16)]).

The following is a set of conclusions after the elimination procedures: (1) In spite of the ambiguities in the estimated numbers (with too many parameters to be set, *intuitively*), the combination of speculations in this subsection and in Subsection 1.4.3 should be regarded as being sound evidence of the non-fluorescent transient species that could be identified with the *hot* benzvalene (which can be excited into S_1 by the probe laser of $\lambda_2 = 272$ nm[4,16)]) or else such as prebenzvalene. (2) The larger contribution of the long-lived species in RE2PI TOF mass spectrometry compared to that assumed for the fluorescence decay, though not thoroughly consistent with the rise of hot benzene, *can* be taken as evidence of a hidden resonance (Sections 1.2, 1.4.3, and 3.2). (3) The long-lived hot benzvalene (or prebenzvalene), which has to be accessible from $\{s\}$, but not counted for $n_{\rm i}$ (Section 3.2), nevertheless non-fluorescent, i.e. with a hint of the transient state for the isomerization might be what is represented as a group of wavefunctions to form a wavepacket near the saddle point, to say more specific, a standing wave trapped in the torus of benzvalenes[1a)] (Subsection 4.1.2 ; or prebenzvalenes). From all this, the density of the resonances, observed and hidden put together, can be assumed to be close to that of the *dark* levels, larger than the estimated value based on the spectral data. It would be rather close to that on the DBO potential surface (Section 2.4). Almost equivalently, the final state for the decay of the *allowed* s_0 state is believed to be the $\{i\}$ states, where the $\{s\}$ state work as intermediate (virtual) states for perturbation, though the s_0–$\{s\}$–$\{i\}$ scheme may partially survive (Subsection 4.1.2).

4.2.3. Deuterium Isotope Effect.[9b)] Not much can be discussed about the D effect described in Section 1.3, except for pointing out the faster rise in the density of states along with an increase in the excess energy in the D substituted compound than that without D substitution.[20d] Namely, even right after the onset of Channel 3, the statistical limit is attained due to a sufficient density of states for both $\{s\}$ and $\{i\}$ (and for $\{c\}$): All of the light level is coupled to more than one nearby dark state, and so on. This would allow the smooth sequential $S_1 \rightsquigarrow X \rightsquigarrow S_0$ decay process. This may also be a reason for the *possible* difficulty in measuring the high-resolution spectra of the D substituted benzenes at the Channel 3 region (with no report in literature) just like the case in the azines (with only one report[20d] ?). By the way, symmetry numbers of perdeuterated benzene are counted to be $\sigma_n = \sigma_r = 6$, the same as those of perprotonated benzene.[20d]

4.3. Transient States Assessed to Exist. In contrast to the simple scheme set in Section 3.1, the observed data indicate rather complex Channel 3 phenomena dependent on the experimental conditions. In concluding this Section 4, the presumed (observed) transient states are listed below: (1) The doorway state N_g as defined in the first paragraph of Section 3.2.[20b] As stated in Subsection 4.2.2, the short-lived component (0.25 ns) of the biexponential decay has to be ascribed mostly to this state (s_0) with slight contribution from the $\{s\}$ states, though we have to assume hidden resonances to which it dephases. If the number of the *bright* resonances, n_s, is large enough, this would be observed as (not so fast) IVR followed by the very fast decay processes (in view of kinetics, Section 3.2). Actually, the *single* exponential decay observed at higher excess energy (> 4500 cm^{-1})[9a] can easily be interpreted assuming this situation of the statistical limit. (2) The bright (observed) resonances described as the forbidden components with distributed lifetimes τ_f's ($\log(\tau_f/\mathrm{ns}) = 0 \sim 1$) for the $6^1 1^3$ state.[7c] (3) The non-fluorescent transient species assessed to be observed with lifetimes τ's ($\log(\tau/\mathrm{ns}) \approx 0.5$) for the $6^1 1^3$ state.[9a,9c,16] This is believed to be ascribed to *hidden* resonances, though not fully, i.e. most probably to the hot benzvalene or less probably to (hot) prebenzvalene, considering the estimated density of states (Section 3.2).

5. Concluding Remarks

In concluding this paper, one comment should be made concerning the proposal by Riedle et al.,[7] as illustrated by their Fig. 4 in Ref. 7b that appears to be approved by Hornburger et al.[11] and Rashev.[17] Actually, their scheme is what can be described by the present theory, just by removing $\{i\}$ from the scheme, i.e. by replacing $\{i\}$ in Fig. 1 with $\{c\}$. Thus, N_s+1 resonances with distributed peak locations $\{E_j\}$ and widths $\{\Gamma_j\}$ as defined by Eqs. 23 in Part II are predicted. Different from the case of pyrazine ($-d_0$; not $-d_4$)[17] these resonances might be overlapped with one another, though no evidence of the interference like the Fano effect to exhibit the asymmetric line shapes is noted so far.[7] The observed lines on the broad background in the high-resolution spectra could be easily interpreted by resonances with exceptionally small widths, Γ_j. The most significant drawback in their scheme was the difficulty in interpreting the predicted density of states, ρ_v. However, this difficulty can be easily removed by introducing the isomer levels into the scheme, either directly or indirectly. Namely, N_s+1 is now replaced by $N_s+N_i-n_i+1$ (Section 3.2).

Through Sections 3 and 4, the Channel 3 problem is successfully answered in a self-consistent form. However, questions still remain especially on the details. For example, even the nature of the (allowed) resonance, e.g. whether it is on the DBO potential or on the ABO potential (Section 3.2), is not well established, though the author's preference is to the latter at least for the allowed component (Subsection 4.2.2). This is probably dependent on the excited energy level, s_0, i.e. on the quantum numbers, v_0 and r_0 (J_0, K_0) (Do not confuse with g_0: Section 3.2), as will be the subject for future study. Also the scheme with the direct coupling of s_0 to $\{i\}$ assisted by the axis-switching (Subsections 4.1.2 and 4.2.1) without passing through or mediated by $\{s\}$ is one of the alternatives that may not be discarded. Though benzvalene (including prebenzvalene) is chosen as a plausible candidate for the intermediate species, the other possibilities may not be completely disregarded. This is almost obvious by just imaging complex multidimensional potential surfaces involving the S_1 and S_0 benzene and the various benzene isomers (never calculated so far). The followings gives conclusions that I derived concerning possible alternative isomers while playing with a molecular model flexible enough to convert into the various benzene isomers *and* keeping the knowledge in the literature such as Refs. 2, 3, 4, 5, 15, 28, and 29 in my mind:

(1) Prefulvene. This appears to be a chemical species with a well-defined biradical-type chemical formula. (If you manipulate a molecular model of benzvalene to convert it into another form of benzvalene, prefulvene may be affirmed as an intermediate transient structure.) However, as discussed in Subsection 4.1.1, it is not stable in view of both the energy and the shape of the (ABO) potential surface. Actually, no evidence of prefulvene is noted in vapor phase, though it could be an intermediate species for the isomerization in the condensed phase (Subsection 4.1.1).

(2) Dewar benzene. This is the strongest alternative to benzvalene. However, the latter was judged to be more probable, as described above, e.g. in Subsection 4.1.2.

(3) Fulvene. This is the most stable benzene isomer (next to benzene). However, isomerization reactions of this molecule *to* and *from* benzene require "rearrangements" of chemical bonds in *both* directions in contrast to the cases of *valence* isomers, i.e., benzvalene and Dewar benzene (with no cleavage of σ bond in the reactions *from* benzene). Therefore, location of a crossing surface of DBO type potential surfaces between benzene and fulvene would be extremely high as was already discussed. (The other isomer has to work as a mediator.)[1,3—5]

As an almost obvious conclusion, more detailed studies concerning both experimental and theoretical aspects, while paying attention to the schemes like that developed here, will be required to obtain further insight into this problem. One of the most desired experiments may be observations of the fluorescence decay curves after excitation into the individual rotational levels using a transform-limited ps laser that played an important role in the case of pyrazine.[20b,30] Then, dephasing into $N_s+N_i-n_i+1$ resonances, for both the allowed and forbidden components, could be detected in the non-exponential decay. Since little information has been obtained for the broad structureless absorption band, i.e. for the forbidden component except for the indirect evidences of the X state, this would be a valuable experiment to perform. As for theory, new kinds of devices, i.e. new kinds of concepts or mathematical formulas should hopefully be developed for a better description, in addition to larger scale computations. In this respect, a "classical wavepacket" dynamics calculation, as applied for benzene, should be noted: Most trajectories after decay via an S_1/S_0 conical intersection were shown to lead back to S_0 benzene without reaching the region of the prefulvene intermediate.[14b] Though this does not take account of the D_{6h}(M) symmetry, it may give some idea complementary to the quantum mechanical description just made above based on the *classical* concepts of radiationless transitions (Subsection 4.1.2).

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