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The Excess Energy Dependence of the Nonradiative Rate

Influence of the non-Condon Effect in C_6H_6 and C_6D_6

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ABSTRACT

Nonradiative rate calculations were made in the non- Condon scheme for the internal conversion transition $S_1 \rightsquigarrow S_0$ in benzene and deuterobenzene. Single vibronic level rate and communicating states rate calculations show the non-Condon effect on the S_1 excess energy dependence. Furthermore, a generating function formalism is developed which allows non-radiative transitions to be described in a coupled three level scheme model.

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Kurzfassung:

In dieser Arbeit werden nichstrahlende Raten unter Anwendung des nicht-Condon Konzepts berechnet. Basierend auf der Brillouin- Wigner Störungstheorie wird die Rate für ein Zweizustandssystem hergeleitet und die zur Vereinfachung notwendigen Näherungen diskutiert. Für die interne Konversion in Benzol und in deuteriertem Benzol untersuchten wir die Überschussenergieabhängigkeit im angeregten elektronischen Singulett-Zustand S_1.

Es werden nichtstrahlende Raten sowohl durch Berechnung des Zerfalls einzelner diskreter vibronischer Niveaus ermittelt als auch durch Bestimmung des Zerfalls aus kommunizierenden Zuständen d. h. aus einem Ensemble isoenergetischer Zustände, die gemäss der kanonischen Verteilung statistisch gewichtet sind.

Diese Rechnungen sind als Ergänzung zu den Arbeiten

a) Influence of "bath" modes on the non-Condon effect (C. P. L. 143 (1988) 284),

und

b) Nonradiative transitions in benzene. III Influence of the non-Condon effect on the excess energy dependence of the rate.

aufzufassen. Zwar zeigen die non-Condon Effekte für alle Moden, die jeweils im non-Condon Schema behandelt werden, gegenüber früheren Arbeiten, die Faktoren zwischen 100 und 1000 ergaben, einen wesentlich kleineren Faktor von etwa 2-5. Andererseits findet man eine modenspezifisch stark unterschiedliche Änderung des non-Condon zu Condon Ratenverhältnisses, wenn die Überschussenergie variiert wird. Die deshalb detailliert in den jeweiligen Tabellen aufgeführten Ergebnisse

zeigen offensichtlich nichttriviale Unterschiede.

Weiterhin werden in dieser Arbeit auch die Rate für ein elektronisches Dreizustands-modell hergeleitet. Zugrunde liegt die Vorstellung eines nichtstrahlenden Zerfalls

a) aus dem S_1, wenn dieser an einen höheren Zustand S_2 koppelt. Insbesondere interessiert die Kopplung an den elektronischen Zustand mit der Symmetrie A_{2u} , wobei die koppelnde Mode die out-of-plane Schwingung ν_4 ist.

b) aus dem S_1 wenn dieser an einen Triplett-zustand gekoppelt ist.

c) aus dem T_1 wenn dieser an höhere Tripletts ankoppelt.

Dazu werden die entsprechenden erzeugenden Funktionen für harmonische Oszillatoren hergeleitet bei der die vibronischen Ausgangszustände zu verschiedenen elektronischen Zuständen gehören.

Schliesslich wurde, um das unterschiedliche Verhalten der Raten in der Condon und nicht-Condon Näherung zu erklären, die Abhängigkeit der einzelnen, die Rate bestimmenden Terme, von dem Sattelpunktsparameter τ untersucht. Hierzu gehören die Zustandssumme, deren Ableitung , der Mittelwert der Energie und deren zweite Ableitung, das mittlere Schwankungsquadrat der Energie.

I. Introduction

Theoretical explanations of polyatomic molecular spectra often fail if one starts from a Condon approximation scheme. Especially nonradiative rates of aromatic molecules were unpredictable with respect to either the absolute values of the rates or to the variation of the rates with increasing excess energy in the excited states[1-6]. Many investigators have therefore assumed that the experimental effects have to be explained by introducing a non-Condon scheme in the theoretical description of the nonradiative decay[7-22].

In particular, it was attempted to interpret the so-called "channel-three" phenomenon in benzene by a non-Condon effect. This is a known general property in aromatic molecules which takes the form of a sharp increase of the nonradiative rates at higher excess energies and a simultaneous diffuseness of the absorption and emission spectra by a non-Condon effect[23-35].

The résumé of these theoretical works is that the non-Condon model may lead to nonradiative rates from the S_1 state of benzene which are about two to three orders of magnitude higher than those in the Condon scheme[7,9].

On the other hand, one finds that the deviations of the experimental results and these calculations were still unsatisfactory. In these rate calculations the pure electronic matrix element taken at an equilibrium nuclear position is supposed to be $\left|V_{IC}^{el}\right|^2 \approx 10^8$ in benzene.

Therefore more elaborate theoretical models were sought[36-43]. While most of these treatments are based on a two electronic state model very recently a third electronic state was introduced by Sobolewski et al.[44,45] to explain the experimental phenomena.

Therfore also in this work the non-Condon formalism is extended to a three electronic states model. As in recent work[46] one applies the communicating states model of Fischer and Schlag[47] and Fischer and Metz[48]. It is especially of some interest if the channel-three mechanism which was suggested to be correlated with the out-of-plane modes, especially with the ν_4 mode[49–52] receives new aspects by the introduction of the non-Condon scheme.

In a further study it is investigated whether nuclear potential crossing of the totally symmetric CH (CD)- stretch vibration as releasing mechanism for strong nonradiative decay[21] is operative in benzene and deuterobenzene. This treatment is extended to cases beyond harmonic approximations by introducing Morse potentials or a local mode concept.

The following includes also supplementary results to Ref.[46]. The few examples of non-Condon rate calculations presented in that work[46] might possibly lead to the objection that the results are mainly due to the special selection of the modes treated in the non-Condon scheme. Therefore a more profound study of the mechanism which most probably give rise to the new non-Condon results should be joined.

Similar as in Ref.[46] one treats only one single mode within the non-Condon scheme, whereas the influence of all the other modes on the non-Condon terms is supposed to be negligible. However, the inclusion of all modes preserves the statistical limit condition which underlies the rate calculation by the saddle point method[1,53]. The derivation of the nonradiative rate expressions is based on models involving two or three electronic states, harmonic normal modes and linear vibronic coupling.

II. The two- and three-electronic-state model

In this section an expression for the nonradiative rates is presented in terms of the corresponding generating function in the non-Condon scheme. For higher energy gaps and in the weak coupling case one can start from the Brillouin-Wigner perturbation theory to describe the wave functions and the energies[7,54-61]. This perturbation theory is characterized so that it derives the wave functions and ABO energies in reciprocal differences of implicit ABO energies and of energies defined at an equilibrium normal coordinate position (zero-order energies) :

$$|\varphi_i(\mathbf{r},\mathbf{Q})>=N_i(\mathbf{Q})\sum_{\{f\}} Res_{\epsilon(\mathbf{Q})=E_i(\mathbf{Q})} <\varphi_f(\mathbf{r},\mathbf{Q_0})\,|R\,(\epsilon(\mathbf{Q}))|\,\varphi_i(\mathbf{r},\mathbf{Q_0})> \\ |\varphi_f(\mathbf{r},\mathbf{Q_0})> \quad . \tag{2.1}$$

The resolvent R($\epsilon(\mathbf{Q})$) and the normalization $N_i(\mathbf{Q})$ are of the forms

$$R\,(\epsilon(\mathbf{Q})) = \frac{1}{\hat{H}^0 - \epsilon(\mathbf{Q})} - \frac{1}{\hat{H}^0 - \epsilon(\mathbf{Q})}\,\bar{U}\,R\,(\epsilon(\mathbf{Q})) \quad , \tag{2.2}$$

$$N_i(\mathbf{Q}) = [<\varphi_i(\mathbf{r},\mathbf{Q_0})|\varphi_i(\mathbf{r},\mathbf{Q})>]^{-\frac{1}{2}} \quad , \tag{2.3}$$

Res are the residues at $\epsilon(\mathbf{Q}) = E_i(\mathbf{Q})$, and

$$\bar{U} = U(\mathbf{r},\mathbf{Q}) - U(\mathbf{r},\mathbf{Q_0}) \quad , \tag{2.4}$$

where $U(\mathbf{r},\mathbf{Q})$ is the potential, and the zeroth-order solution is obtained by

$$\hat{H}_0\,|\varphi_i(\mathbf{r},\mathbf{Q_0})>= E_i(\mathbf{Q_0})|\,\varphi_i(\mathbf{r},\mathbf{Q_0})> \quad , \tag{2.5}$$

$$\hat{H}_0 = \hat{T}_r + U(\mathbf{r},\mathbf{Q_0}) \quad , \tag{2.6}$$

where $\hat{T}_r$ is the operator of the electronic kinetic energy.

In a model system which assumes a finite number of states the infinite terms in Eqs. (2.1) - (2.3) can be given in closed form if it is assumed that zeros of the denominators in Eq. (2.2) can be excluded. The adiabatic wave functions for the three-level system in the most general case, where all states are coupled with one another, are obtained as follows:

$$
\begin{aligned}
|\varphi_s(\mathbf{r},\mathbf{Q})> = N_s(\mathbf{Q}) \Bigg\{ |\varphi_s^0> + \\
& \Bigg[\frac{<\varphi_s^0\left|\bar{U}\right|\varphi_k^0> \; [E_s(\mathbf{Q})-\bar{E}_k(\mathbf{Q})]}{[E_s(\mathbf{Q})-\bar{E}_k(\mathbf{Q})]\;[E_s(\mathbf{Q})-\bar{E}_l(\mathbf{Q})]-\left|<\varphi_l^0\left|\bar{U}\right|\varphi_k^0>\right|^2}+ \\
& \frac{<\varphi_s^0\left|\bar{U}\right|\varphi_l^0><\varphi_l^0\left|\bar{U}\right|\varphi_k^0>}{[E_s(\mathbf{Q})-\bar{E}_k(\mathbf{Q})]\;[E_s(\mathbf{Q})-\bar{E}_l(\mathbf{Q})]-\left|<\varphi_l^0\left|\bar{U}\right|\varphi_k^0>\right|^2}\Bigg] \\
& \times\;|\varphi_k^0> + \\
& \Bigg[\frac{<\varphi_s^0\left|\bar{U}\right|\varphi_l^0> \; [E_s(\mathbf{Q})-\bar{E}_k(\mathbf{Q})]}{[E_s(\mathbf{Q})-\bar{E}_k(\mathbf{Q})]\;[E_s(\mathbf{Q})-\bar{E}_l(\mathbf{Q})]-\left|<\varphi_l^0\left|\bar{U}\right|\varphi_k^0>\right|^2}+ \\
& \frac{<\varphi_s^0\left|\bar{U}\right|\varphi_k^0> < \varphi_k^0\left|\bar{U}\right|\varphi_l^0>}{[E_s(\mathbf{Q})-\bar{E}_k(\mathbf{Q})][E_s(\mathbf{Q})-\bar{E}_l(\mathbf{Q})]-\left|<\varphi_l^0\left|\bar{U}\right|\varphi_k^0>\right|^2}\Bigg] \\
& \times\;|\varphi_l^0>\Bigg\}\;,
\end{aligned}
\tag{2.7}
$$

where s, k, l have to be replaced by f, i, j and cyclical permutations. Subscript j denotes the second excited electronic state.

A considerable simplification can be obtained if one assumes $V_{jf} \approx 0$, which means that the coupling of the higher excited electronic state to the ground state can be neglected. The expression for the wave functions (Eq.(2.7)) is still too complicated for direct evaluation of the rate. More elaborate approximations for the special model situations should therefore be introduced. In the case of benzene or deuterobenzene, for example, a coupling of the S_1 and the A_{2u} states, where the coupling mode is the ν_4, should be of some interest. For these molecules it can be additionally assumed that

$$
|<\varphi_i^0\left|\bar{U}\right|\varphi_f^0>|^2/\;\left[E_f(\mathbf{Q})-\bar{E}_i(\mathbf{Q})\right]\ll 1\quad,\Delta E_{if}\gg 1\;. \tag{2.8}
$$

Equation (2.7) may then be simplified to

$$|\varphi_l(\mathbf{r},\mathbf{Q})> = N_l(\mathbf{Q}) \left\{ |\varphi_l^0> + \frac{<\varphi_s^0 \left|\bar{U}\right| \varphi_l^0>}{E_l(\mathbf{Q}) - \bar{E}_s(\mathbf{Q})} |\varphi_s^0> + \right. \\ \left. \frac{<\varphi_k^0 \left|\bar{U}\right| \varphi_s^0> <\varphi_s^0 \left|\bar{U}\right| \varphi_l^0>}{\left[E_l(\mathbf{Q}) - \bar{E}_k(\mathbf{Q})\right] \left[E_l(\mathbf{Q}) - \bar{E}_s(\mathbf{Q})\right]} |\varphi_k^0 \right\} . \tag{2.9}$$

For the self-consistency relation one finds

$$E_j(\mathbf{Q}) + E_i(\mathbf{Q}) + E_f(\mathbf{Q}) = \bar{E}_j(\mathbf{Q}) + \bar{E}_i(\mathbf{Q}) + \bar{E}_f(\mathbf{Q}) \quad , \tag{2.10}$$

where the adiabatic energies are derived from the eigenvalue equation

$$\left[\hat{H} - E(\mathbf{Q})\ \hat{I}\right] = \hat{0} \ . \tag{2.11}$$

$\hat{H}$ is of the form ($<\varphi_f^0 \left|\bar{U}\right| \varphi_i^0>$ is abbreviated to V_{fi}^c)

$$\hat{H} = \hat{T} + \begin{pmatrix} \bar{E}_f & V_{fi}^c & V_{fj}^c \\ V_{if}^c & \bar{E}_i & V_{ij}^c \\ V_{jf}^c & V_{ji}^c & \bar{E}_j \end{pmatrix} \tag{2.12}$$

In the special case of a two-level system one obtains[7,57]

$$|\varphi_i(\mathbf{r},\mathbf{Q})> = \left[|\varphi_i^0> + \frac{<\varphi_f^0 \left|\bar{U}\right| \varphi_i^0>}{E_i(\mathbf{Q}) - \bar{E}_f(\mathbf{Q})} |\varphi_f^0> \right] N_i(\mathbf{Q}) \ , \\ |\varphi_f(\mathbf{r},\mathbf{Q})> = \left[|\varphi_f^0> + \frac{<\varphi_i^0 \left|\bar{U}\right| \varphi_f^0>}{E_f(\mathbf{Q}) - \bar{E}_i(\mathbf{Q})} |\varphi_i^0> \right] N_f(\mathbf{Q}) \ , \tag{2.13}$$

$$N_i(\mathbf{Q}) = \left[1 + \frac{\left|<\varphi_f^0 \left|\bar{U}\right| \varphi_i^0>\right|^2}{\left|E_i(\mathbf{Q}) - \bar{E}_f(\mathbf{Q})\right|^2} \right]^{-\frac{1}{2}} \ , \tag{2.14}$$

$$E_i(\mathbf{Q}) = \bar{E}_i(\mathbf{Q}) + \frac{\left|<\varphi_f^0 \left|\bar{U}\right| \varphi_i^0>\right|^2}{E_i(\mathbf{Q}) - \bar{E}_f(\mathbf{Q})} \ , \tag{2.15}$$

where $E_{i,f}(\mathbf{Q})$ are the adiabatic and $\bar{E}_{i,f}(\mathbf{Q})$ the zeroth-order nuclear potentials, and $\varphi_{i,f}(\mathbf{r},\mathbf{Q}_0)$ is abbreviated to $\varphi_{i,f}^0$. As can easily be seen from Eqs.(2.13)-(2.15) in the Brillouin-Wigner perturbation scheme, the wave functions and the normalization $N_{i,f}(\mathbf{Q})$ are functions of all normal coordinates. An analysis of Eq.(2.13) shows that whenever crossings of the potential energies in the denominator occur this ansatz breaks down. However, in general this should be an artificial effect. The exact potential, which is only known in a few cases , e.g. for very small molecules with few electrons, should also approach zero so that one has a removable discontinuity. For polyatomic molecules and in the weak coupling case it is assumed that in the perturbation treatment $\bar{U}$ (Eq.(2.4)) can be approximated by linear terms of the normal coordinates:

$$\bar{U} \approx \bar{U}' = \sum_k \left. \frac{\partial U(\mathbf{r},\mathbf{Q})}{\partial Q_k} \right|_{Q_k=Q_k^0} Q_k \quad . \qquad (2.16)$$

It is obvious from Eq.(2.15) that the adiabatic potentials lead in general to a system of N-dimensional coupled differential equations for the nuclear wave functions and energy eigenvalues:

$$\left[\hat{T}_N + E_{i,f}(\mathbf{Q})\right] \; |\Lambda_{i,f}(\mathbf{Q})> = \epsilon_{i,f}|\Lambda_{i,f}(\mathbf{Q})> \quad , \qquad (2.17)$$

where $\hat{T}$ is the nuclear kinetic energy operator $\hat{T} = -\frac{1}{2}\sum_{k=1}^{N} \frac{\partial^2}{\partial Q_k^2}$. In nonradiative transition processes these couplings may lead to enormous effects because very high quantum numbers are involved. Especially these couplings may be the apparatus by which energy can "communicate"[5,44,62–64]. The quantum system of coupled oscillators, particularly with regard to the classical quantum correspondence and possible manifestations of the onset of classical chaos in quantum level spectra and dynamics, has been investigated by Noid et al.[54], Rice[65], Ezra[66] and many others[58,67–70]. It is obvious that these questions have immediate relevance to theories of intramolecular energy flow. Also very close to this question, Amat[62] investigated the effective harmonic potentials and the effective normal coordinates.

To obtain a decoupling in Eq.(2.17) one derives the adiabatic potentials $E_{i,f}(\mathbf{Q})$ at $\mathbf{Q} = \mathbf{0}$ to second order. Thus all zero- order potentials $E_{i,f}(\mathbf{Q})$ and approximated adiabatic potentials $E^*_{i,f}(\mathbf{Q})$ are equal, with the exception of the "promoting mode" . This is true as long as only the derivatives of $U(\mathbf{r},\mathbf{Q})$ with respect to the "promoting mode" Q_p are regarded as non-zero:

$$E^*_{i,f}(Q_p) = \bar{E}_{i,f}(Q_p) \pm \left. \frac{\left| < \varphi_f^0 \left| \bar{U} \right| \varphi_i^0 > \right|^2}{\bar{E}_i(\mathbf{Q}) - \bar{E}_f(\mathbf{Q})} \right|_{\mathbf{Q}=\mathbf{0}} Q_p^2 \quad . \tag{2.18}$$

III. The decay rate expression

Decay theories of coupled unstable states have been a matter of serious concern in recent years[71-76]. The nonradiative decay rate is expressed by

$$k_{nr} = \frac{2\pi}{\hbar} \sum_{\{f\}} \left| V_{if}(\mathbf{Q}) \right|^2 \delta(E_i - E_f) \quad . \tag{3.1}$$

According to Eq.(2.9) one obtains for a three-level system:

$$V_{if}(\mathbf{Q}) =< \Lambda_f(\mathbf{Q}) \left| L_{if}^{(3)}(\omega) \right| \Lambda_i(\mathbf{Q}) > \quad , \tag{3.2}$$

$$\begin{aligned} L_{if}^{(3)}(\omega) &= < \varphi_f(\mathbf{r},\mathbf{Q})| \left[\hat{T}_N, |\varphi_i(\mathbf{r},\mathbf{Q}) > \right] = \\ & N_f(\mathbf{Q}) \left\{ \left[\hat{T}_N, \frac{< \varphi_f^0 \left| \bar{U} \right| \varphi_i^0 >}{E_i(\mathbf{Q}) - \bar{E}_f(\mathbf{Q})} \right] + \right. \\ & \frac{< \varphi_i^0 \left| \bar{U} \right| \varphi_f^0 >}{E_f(\mathbf{Q}) - \bar{E}_i(\mathbf{Q})} \left[\hat{T}_N, N_i(\mathbf{Q}) \right] + \\ & \frac{< \varphi_j^0 \left| \bar{U} \right| \varphi_i^0 >< \varphi_i^0 \left| \bar{U} \right| \varphi_f^0 >}{\left[E_f(\mathbf{Q}) - \bar{E}_i(\mathbf{Q}) \right] \left[E_f(\mathbf{Q}) - \bar{E}_j(\mathbf{Q}) \right]} \\ & \left. \times \left[\hat{T}_N, \frac{< \varphi_i^0 \left| \bar{U} \right| \varphi_j^0 >}{E_i(\mathbf{Q}) - \bar{E}_j(\mathbf{Q})} N_i(\mathbf{Q}) \right] \right\} \quad . \end{aligned} \tag{3.3}$$

For the internal conversion decay in a two-level model $V_{if}(\mathbf{Q})$ is of the form

$$\begin{aligned} V_{if}(\mathbf{Q}) &= < \Lambda_f(\mathbf{Q}) \left| L_{if}(\omega) \right| \Lambda_i(\mathbf{Q}) >= \\ & - \sum_k \omega_k \left\{ < \Lambda_f(\mathbf{Q}) \right| \left[< \varphi_f(\mathbf{r},\mathbf{Q}) \left| \frac{\partial}{\partial Q_k} \right| \varphi_i(\mathbf{r},\mathbf{Q}) > \frac{\partial}{\partial Q_k} + \right. \\ & \left. \left. \frac{1}{2} < \varphi_f(\mathbf{r},\mathbf{Q}) \left| \frac{\partial^2}{\partial Q_k^2} \right| \varphi_i(\mathbf{r},\mathbf{Q}) > \right] \middle| \Lambda_i(\mathbf{Q}) > \right\} \quad . \end{aligned} \tag{3.4}$$

Inserting $\varphi_{i,f}(\mathbf{r}, \mathbf{Q})$ and $E_{i,f}(\mathbf{Q})$ from Eqs.(2.13)-(2.15), one obtains

$$L_{if}(\omega) = -\sum_k \omega_k N_f(\mathbf{Q}) \Bigg\{ \frac{\partial}{\partial Q_k} \left[\frac{< \varphi_f^0 \left| \bar{U} \right| \varphi_i^0 >}{E_i(\mathbf{Q}) - \bar{E}_f(\mathbf{Q})} N_i(\mathbf{Q}) \right] \frac{\partial}{\partial Q_k} + \frac{< \varphi_i^0 \left| \bar{U} \right| \varphi_f^0 >}{E_f(\mathbf{Q}) - \bar{E}_i(\mathbf{Q})} \frac{\partial}{\partial Q_k} [N_i(\mathbf{Q})] \frac{\partial}{\partial Q_k} + \frac{1}{2} \frac{\partial^2}{\partial Q_k^2} \left[\frac{< \varphi_f^0 \left| \bar{U} \right| \varphi_i^0 >}{E_i(\mathbf{Q}) - \bar{E}_f(\mathbf{Q})} N_i(\mathbf{Q}) \right] + \frac{1}{2} \frac{< \varphi_i^0 \left| \bar{U} \right| \varphi_f^0 >}{E_f(\mathbf{Q}) - \bar{E}_i(\mathbf{Q})} \frac{\partial^2}{\partial Q_k^2} [N_i(\mathbf{Q})] \Bigg\} . \tag{3.5}$$

The derivatives in Eq.(3.5) must act only on the expressions in square brackets.

For the actual calculation of the nonradiative rates one uses the generating function formalism relating to k_{nr} of Eq.(3.1) . This can be obtained by taking the Fourier transform of the δ-function :

$$k_{nr} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} L_{if}(t) dt . \tag{3.6}$$

In the general case $L_{if}(t)$ is a function $f(\bar{L}_{if}(t))$, where f depends on the special model chosen:

$$\bar{L}_{if}(t) = < \Lambda_i \left| e^{-i\hat{H}_i t/\hbar} L_{if}(\omega) e^{i\hat{H}_f t/\hbar} L_{jf}^{+}(\omega) \right| \Lambda_j > , \tag{3.7}$$

where $\hat{H}_i$ and $\hat{H}_f$ are the corresponding Hamilton operators for the initial state i and final state f and $\bar{L}_{jf}(\omega)$ is obtained from $\bar{L}_{if}(\omega)$ when i is exchanged with j. The time integration in Eq.(3.6) is performed by the saddle-point approximation[77].

After some mathematical transformations and approximations of the generating function $L_{if}(t)$[77] one gets for the two-electronic-state model the following expression as a function of the saddle point parameter τ:

$$k = \sqrt{2\pi} \frac{Z(\tau)}{\left[< h^2(\tau) > - < h(\tau) >^2 \right]^{\frac{1}{2}}} . \tag{3.8}$$

If anharmonic mode mixing etc. are excluded, the following definite equations are obtained for $Z(\tau)$, $< h(\tau) >$ and $< h^2(\tau) >$ as functions of N single vibrational product terms $Z_k(\tau)$, $< h_k(\tau) >$ and $< h_k^2(\tau) >$:

$$Z(\tau) = \prod_{k=1}^{N} Z_k(\tau) \; exp\Big(\frac{-\Delta E \; \tau}{\hbar}\Big) \; ,$$

$$\Delta E = E_i^0 - E_f^0 \; , \tag{3.9}$$

$$< h(\tau) > = \sum_{k=1}^{N} < h_k(\tau) > - \frac{\Delta E}{\hbar} \; , \tag{3.10}$$

$$< h^2(\tau) > = \sum_{k=1}^{N} < h_k^2(\tau) > \; , \tag{3.11}$$

where k refers to the k-th vibration. The generating function $\bar{L}_{if}(t)$ (Eq.(3.7)) yields

$$Z_k(\tau) = < \tilde{n}| e^{i\tilde{p}_k \tilde{\Delta}_k} \; e^{-\hat{H}_{i,k} \; \tau/\hbar} \; L_{if}(\omega_k) \; e^{\hat{H}_{f,k} \; \tau/\hbar} \; L_{if}^{+}(\omega_k) \; e^{-i\check{p}_k \check{\Delta}_k} \; |\check{n} > \quad . \tag{3.12}$$

$\tilde{p}_k, \check{p}_k$ and $\tilde{\Delta}_k, \check{\Delta}_k$ denote the momentum operators and the displacements of the potential surfaces, respectively. To simplify, the tilde and the hook are introduced as substitution for subscripts i and j, respectively, whereas subscript f is dropped. In the next section and Appendix B for the terms occurring in $Z_k(\tau)$ and in the partial derivatives $\frac{\partial Z_k(\tau)}{\partial \tau}$ and $\frac{\partial^2 Z_k(\tau)}{\partial \tau^2}$ closed-form expressions are derived:

$$< h_k(\tau) > = \frac{\partial \ln Z_k(\tau)}{\partial \tau} \; , \tag{3.13}$$

$$< h_k^2(\tau) > = \frac{\partial^2 \ln Z_k(\tau)}{\partial \tau^2} \; . \tag{3.14}$$

IV. Calculation procedure

In this work the energy denominator of the non-Condon formalism will actually be treated one-dimensionally, while multidimensional examples will be presented in forthcoming publications[78] .

A multidimensional crossing point will lead to a non-removable discontinuity and cannot be treated exactly in the adiabatic approximation. In this case more elaborate formalisms of Heider and Fischer[40] , Child and Halonen[79] and many others[80,81] have to be applied.

For calculating non-Condon rates according to Eq.(3.6) one has to evaluate a non-Condon propagator of the following structure (harmonic potentials) :

$$T_{i\tilde{\mathbf{n}},j\check{\mathbf{n}}} = < \tilde{\mathbf{n}} \left| \frac{1}{\xi_i^+} e^{\hat{H}_f \tau/\hbar} \frac{1}{\xi_j} \right| \check{\mathbf{n}} > \quad , \tag{4.1}$$

where $\xi_{i,j}$ is the difference of the adiabatic energy $E(\omega, \mathbf{Q})$ or of the approximate adiabatic energy and the zero-order energies $\bar{E}(\omega, \mathbf{Q})$:

$$\begin{aligned} \xi_{i,j} =& E_{i,j}(\omega, \mathbf{Q}) - \bar{E}_f(\omega, \mathbf{Q}) = \\ & \Delta E + \frac{1}{2} \sum_{k=1}^{N} [\omega_{i,j;k}(Q_{i,j;k} - \Delta_{i,j;k})^2 - \omega_{f,k} Q_k^2] \quad , \end{aligned} \tag{4.2}$$

where henceforth the tilde and hook refer to first and second excited electronic state terms. For harmonic and displaced potentials the $\xi_{i,j}$ are of the form (in the following only the terms for ξ_i are expanded; ξ_j terms are structurally identical; thus only the tilde has to be replaced by the hook to find the corresponding ξ_j expression.)

$$\tilde{\xi} = \tilde{\Delta E}' - \tilde{\gamma}\tilde{\omega}\tilde{Q} + \tilde{\delta}\tilde{\omega}\tilde{Q}^2 \quad , \tag{4.3}$$

$$\tilde{\Delta E}' = \Delta E + \frac{1}{2}\,\tilde{\omega}\tilde{\Delta}^2 \quad .$$

If crossing points occur, then $1/\tilde{\xi}$ can be rewritten :

$$
\begin{aligned}
\frac{1}{\tilde{\xi}} &= -\frac{\tilde{\gamma}}{|\tilde{\gamma}|} \frac{1}{\sqrt{1-\frac{4\tilde{\delta}\tilde{\Delta}E'}{\tilde{\gamma}^2\tilde{\omega}}}} \left[\frac{1}{\tilde{\gamma}\tilde{Q}_1 - \tilde{\gamma}\tilde{Q}} - \frac{1}{\tilde{\gamma}\tilde{Q}_2 - \tilde{\gamma}\tilde{Q}} \right] , \\
\tilde{Q}_{1,2} &= \frac{1}{2\tilde{\delta}} \left[\tilde{\gamma} \pm \sqrt{\tilde{\gamma}^2 - \frac{4\tilde{\delta}\tilde{\Delta}E'}{\tilde{\omega}}} \right] , \\
& \tilde{\gamma}^2 - \frac{4\tilde{\delta}\tilde{\Delta}E'}{\tilde{\omega}} > 0 .
\end{aligned} \tag{4.4}
$$

Furthermore, one uses the identity

$$
\frac{1}{y - \tilde{\gamma}\tilde{Q}} = \mathbf{P} \quad \frac{1}{y - \tilde{\gamma}\tilde{Q} - i\eta} = i \, \Im \int_0^\infty e^{-i\left(y - \tilde{\gamma}\tilde{Q}\right)t} \; dt , \tag{4.5}
$$

where $\mathbf{P}$ means the principal value. To evaluate $Z_k(\tau)$ in Eq.(3.12), it is very convenient to introduce the creation and annihilation operators b, b^+ and $\tilde{b}, \tilde{b}^+$, $\check{b}$, $\check{b}^+$ for the ground and excited states :

$$
\begin{aligned}
Q &= \frac{1}{\sqrt{2}} \left(b + b^+ \right) , \quad \tilde{Q} = \frac{1}{\sqrt{2}} \left(\tilde{b} + \tilde{b}^+ \right) , \quad Q = \sqrt{\frac{\omega}{\tilde{\omega}}} \, \tilde{Q} , \\
\check{Q} &= \frac{1}{\sqrt{2}} \left(\check{b} + \check{b}^+ \right) , Q = \sqrt{\frac{\omega}{\check{\omega}}} \, \check{Q} , \\
\frac{\partial}{\partial Q} &= ip = \frac{1}{\sqrt{2}} \left(b - b^+ \right) , \quad \frac{\partial}{\partial \tilde{Q}} = i\tilde{p} = \frac{1}{\sqrt{2}} \left(\tilde{b} - \tilde{b}^+ \right) , \\
\frac{\partial}{\partial \check{Q}} &= i\check{p} = \frac{1}{\sqrt{2}} \left(\check{b} - \check{b}^+ \right) ,
\end{aligned}
$$

and the relations

$$
\begin{aligned}
\tilde{b} &= \tilde{\alpha} b - \tilde{\beta} b^+ , \quad \tilde{b}^+ = \tilde{\alpha} b^+ - \tilde{\beta} b , \\
\tilde{\alpha} &= \frac{\omega + \tilde{\omega}}{2\sqrt{\omega\tilde{\omega}}} , \quad \tilde{\beta} = \frac{\omega - \tilde{\omega}}{2\sqrt{\omega\tilde{\omega}}} ,
\end{aligned} \tag{4.6}
$$

where ω, $\tilde{\omega}$ and $\check{\omega}$ are the corresponding frequencies.

If no crossing points occur, Eq.(4.1) can be written $(\tilde{\delta} \neq 0)$

$$
\tilde{\xi} = \frac{\tilde{\omega}}{\tilde{\delta}} \left[\left(\tilde{\delta}\tilde{Q} - \frac{\tilde{\gamma}}{2} \right)^2 + \frac{\tilde{\delta}\tilde{\Delta}E'}{\tilde{\omega}} - \frac{\tilde{\gamma}^2}{4} \right] , \tag{4.7}
$$

Applying Laplace transformation[82], one obtains

$$\frac{1}{\tilde{\xi}} = \frac{\tilde{\delta}}{\tilde{\omega}\tilde{\kappa}} \ \Re \int_0^{\infty} e^{\frac{i\tilde{\gamma}t}{2} - \tilde{\kappa}t} \ e^{-i\tilde{\delta}\tilde{Q}t} \ dt \ ,$$

$$\tilde{\kappa} = \sqrt{\frac{\tilde{\delta}\tilde{\Delta}E'}{\tilde{\omega}} - \frac{\tilde{\gamma}^2}{4}} \ . \tag{4.8}$$

To calculate the rate according to Eq.(3.6), one has to evaluate the following terms which are valid for the one-dimensional distorted and/or displaced harmonic oscillator cases.

One has to distinguish between several cases with respect to whether the potentials have crossing points with each other or not. The main cases from which all the others can be derived are developed below.

A) Crossings of the S_0 with the S_1 and S_2 nuclear potentials

From Eqs.(3.12) and (4.4) terms of the following form are derived when, for example, $E_i(\tilde{\omega}, \tilde{Q})$ or $E_j(\check{\omega}, \check{Q})$ crosses $E_f(\omega, Q)$ (the subscripts for the k-th mode are omitted):

$$\begin{aligned} &< \tilde{n} \left| \ e^{i\tilde{p}\tilde{\Delta}} \ \frac{1}{\tilde{\xi}^{+}} \ e^{\hat{H}_f \ \tau/\hbar} \ \frac{1}{\check{\xi}} \ e^{-i\check{p}\check{\Delta}} \ \right| \check{n} >= \\ &\frac{\tilde{\gamma}\check{\gamma}}{N_1} \ \left[W(\tilde{Q}_1, \check{Q}_1) - W(\tilde{Q}_1, \check{Q}_2) - W(\tilde{Q}_2, \check{Q}_1) + W(\tilde{Q}_2, \check{Q}_2)\right] \ , \end{aligned} \tag{4.9}$$

$$\begin{aligned} &W(\tilde{Q}_\sigma, \check{Q}_{\sigma'}) = \\ &< \tilde{n} \left| \ e^{i\tilde{p}\tilde{\Delta}} \frac{1}{\tilde{\gamma}\tilde{Q}_\sigma - \tilde{\gamma}\tilde{Q}} \ e^{\hat{H}_f \ \tau/\hbar} \ \frac{1}{\check{\gamma}\check{Q}_{\sigma'} - \check{\gamma}\check{Q}} \ e^{-i\check{p}\check{\Delta}} \right| \check{n} >= \\ &\int_0^{\infty} \ dt_1 \int_0^{\infty} \ dt_2 \ \left[\ W(t_1, t_2) - W(t_1, -t_2) - W(-t_1, t_2) + W(-t_1, -t_2)\right] \ , \end{aligned}$$

$$N_1 = 4 \left[\left(\tilde{\gamma}^2 - \frac{4\tilde{\delta}\tilde{\Delta}E'}{\tilde{\omega}} \right) \ \left(\check{\gamma}^2 - \frac{4\check{\delta}\check{\Delta}E'}{\check{\omega}} \right) \right]^{\frac{1}{2}} \ , \tag{4.10}$$

$$W(t_1,t_2) = e^{-i\tilde{\gamma}(\tilde{Q}_\sigma - \tilde{\Delta})\, t_1} \; e^{-i\check{\gamma}(\check{Q}_{\sigma'} - \check{\Delta})\, t_2} \; \bar{W}(t_1,t_2) \quad , \tag{4.11}$$

$$\sigma, \sigma' = \{1,2\} \quad ,$$

$$\bar{W}(t_1,t_2) = <\tilde{n}| e^{i\tilde{p}\tilde{\Delta}} \; e^{i\tilde{\gamma}\tilde{Q}t_1} \; e^{\hat{H}_f \tau/\hbar} \; e^{i\check{\gamma}\check{Q}t_2} \; e^{-i\check{p}\check{\Delta}} \; |\check{n}> \quad . \tag{4.12}$$

To evaluate $\bar{W}(t_1,t_2)$, the well-known disentangle rules have to be applied. The strategy is to express all operators in terms of $\tilde{b}^+$ and $\check{b}$ where $\tilde{b}^+$ is transposed to the left and $\check{b}$ to the right, both acting as annihilation operators. For this purpose a series of operator relations have to be introduced. It is useful to present Eq.(4.12) in a slightly different form:

$$\begin{aligned}
&W(t_1,t_2) = \varphi_1 \; U_{\tilde{n},\check{n}}(t_1,t_2) \quad , \\
&U_{\tilde{n},\check{n}}(t_1,t_2) = <\tilde{n}\left| \; e^{i\tilde{\gamma}\tilde{\Delta}t_1} \; \hat{U} \; e^{i\check{\gamma}\check{\Delta}t_2} \; \right| \check{n}> \quad , \\
&\hat{U} = e^{i\tilde{p}\tilde{\Delta}} \; e^{\hat{H}_f \tau/\hbar} \; e^{-i\check{p}\check{\Delta}} \quad , \\
&\varphi_1 = exp\left[i\left(\tilde{\Delta}\tilde{\gamma}t_1 + \check{\Delta}\check{\gamma}t_2 \right) \right] \quad .
\end{aligned} \tag{4.13}$$

The following operator relations are necessary to disentangle Eq.(4.13):

$$e^{-i\omega t b^+ b} \begin{pmatrix} b \\ b^+ \end{pmatrix} e^{i\omega t b^+ b} = \begin{pmatrix} e^{i\omega t} \; b \\ e^{-i\omega t} \; b^+ \end{pmatrix} \quad , \tag{4.14}$$

$$\hat{U}^{-1}(t) \begin{pmatrix} \tilde{b} \\ \tilde{b}^+ \end{pmatrix} \hat{U}(t) = \begin{pmatrix} A \; , & B \\ \bar{B} \; , & \bar{A} \end{pmatrix} \begin{pmatrix} \check{b} \\ \check{b}^+ \end{pmatrix} + \begin{pmatrix} G \\ \bar{G} \end{pmatrix} \quad , \tag{4.15}$$

$$\hat{U}(t) \begin{pmatrix} \check{b} \\ \check{b}^+ \end{pmatrix} \hat{U}^{-1}(t) = \begin{pmatrix} \bar{A} \; , & -B \\ -\bar{B} \; , & A \end{pmatrix} \begin{pmatrix} \tilde{b} \\ \tilde{b}^+ \end{pmatrix} + \begin{pmatrix} \check{\bar{G}} \\ \check{G} \end{pmatrix} \quad , \tag{4.16}$$

$$\begin{pmatrix} \tilde{b} \\ \tilde{b}^+ \end{pmatrix} \hat{U}(t) = \hat{U}(t) \begin{pmatrix} A\check{b} + B\check{b}^+ + G \\ \bar{B}\check{b} + \bar{A}\check{b}^+ + \bar{G} \end{pmatrix} = \hat{U}(t) \begin{pmatrix} c \\ c^+ \end{pmatrix} \quad ,$$

$$\tilde{b}\hat{U}(t) = \hat{U}(t) \; \frac{1}{\bar{A}} \; (\check{b} + Bc^+ - \check{\bar{G}}) \quad , \tag{4.17}$$

$$\begin{aligned}
\hat{U}(t)\check{b} &= \left(\tilde{b}\check{A} - \tilde{b}^+ B + \check{\bar{G}} \right) \; \hat{U}(t) \quad , \\
\hat{U}(t)\check{b}^+ &= \frac{1}{\bar{A}} \left(c^+ - \bar{B}\check{b} - \bar{G} \right) \; \hat{U}(t) \quad , \\
&\left[c^+ , \check{b} \right] = -\bar{A} \quad ,
\end{aligned} \tag{4.18}$$

$$e^{\hat{x}}\ e^{\hat{y}} = e^{\hat{y}}\ e^{\hat{x}}\ e^{[\hat{x},\hat{y}]} \quad . \tag{4.19}$$

$A, \bar{A}, B, \bar{B}, G, \check{G}, \check{\bar{G}}$ are given in Appendix B. These operator relations now allow $U_{\tilde{n},\check{n}}(t_1, t_2)$ in Eq.(4.13) to be evaluated:

$$U_{\tilde{n},\check{n}}(t_1,t_2) = \varphi_2 \ < \tilde{n} \left| \ e^{\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\tilde{b}^+} \ e^{\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\tilde{b}} \ \left|\hat{U}\right| \ e^{\frac{i}{\sqrt{2}}\check{\gamma}t_2\check{b}^+} \ e^{\frac{i}{\sqrt{2}}\check{\gamma}t_2\check{b}} \right| \check{n} > \quad ,$$

$$\varphi_2 = exp\left[-\frac{\tilde{\gamma}^2}{4}t_1^2 - \frac{\check{\gamma}^2}{4}t_2^2\right] \quad . \tag{4.20}$$

By means of the relation in Eq.(4.17) the exponential operator $e^{\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\tilde{b}^+}$ on the left of $\hat{U}$ is transposed to the right:

$$\begin{aligned} U_{\tilde{n},\check{n}}(t_1,t_2) =& \varphi_2\varphi_3 \ < \tilde{n} \left| e^{\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\tilde{b}^+} \ \left|\hat{U}\right| \ e^{\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\frac{1}{\bar{A}}\left(\check{b}+Bc^+-\check{\bar{G}}\right)} \right. \\ & \left. \times \ e^{\frac{i}{\sqrt{2}}\check{\gamma}t_2 \ \frac{1}{\bar{A}}\left(c^+-\bar{B}\check{b}-\bar{G}\right)} \ e^{\frac{i}{\sqrt{2}}\check{\gamma}t_2\check{b}} \right| \check{n} > \quad , \end{aligned} \tag{4.21}$$

$$\varphi_3 = exp\left[-\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\frac{\check{\bar{G}}}{\bar{A}} - \frac{i}{\sqrt{2}}\check{\gamma}t_2\frac{\bar{G}}{\bar{A}}\right] \quad ,$$

$$\begin{aligned} U_{\tilde{n},\check{n}}(t_1,t_2) = & \varphi_1\varphi_2\varphi_3\varphi_4 < \tilde{n} \left| \ e^{\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\tilde{b}^+} \ \left| \ \hat{U} \ \right| \ e^{\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\frac{B}{\bar{A}}c^+} \ e^{\frac{i}{\sqrt{2}}\frac{\tilde{\gamma}t_1}{\bar{A}}\check{b}} \right. \\ & \left. \times \ e^{\frac{i}{\sqrt{2}}\frac{\check{\gamma}t_2}{\bar{A}}c^+} \ e^{-\frac{i}{\sqrt{2}}\frac{\check{\gamma}t_2}{\bar{A}}\bar{B}\check{b}} \ e^{\frac{i}{\sqrt{2}}\check{\gamma}t_2\check{b}} \ \right| \check{n} > \quad , \end{aligned} \tag{4.22}$$

$$\varphi_4 = exp\left[\frac{1}{4\bar{A}}\left(-B\tilde{\gamma}^2t_1^2 + \bar{B}\check{\gamma}^2t_2^2\right)\right] \quad .$$

Ordering the exponential operators in Eq.(4.22), one obtains

$$\begin{aligned} U_{\tilde{n},\check{n}}(t_1,t_2) =& \varphi < \tilde{n} \left| \ e^{\frac{i}{\sqrt{2}}\tilde{\gamma}t_1\tilde{b}^+} \ \left|\hat{U}\right| \ e^{\frac{i}{\sqrt{2}}\frac{1}{\bar{A}}(\tilde{\gamma}Bt_1+\check{\gamma}t_2)c^+} \right. \\ & \left. \times \ e^{\frac{i}{\sqrt{2}}\frac{1}{\bar{A}} \ [\tilde{\gamma}t_1+\check{\gamma}t_2(-\bar{B}+\bar{A})]\check{b}} \right| \check{n} > \quad , \end{aligned} \tag{4.23}$$

$$\varphi = \varphi_1\varphi_2\varphi_3\varphi_4\varphi_5 \quad ,$$

$$\varphi_5 = e^{-\frac{\tilde{\gamma}\check{\gamma}}{2\bar{A}}t_1t_2} \quad .$$

Transforming the exponential term with c^+ to the left finally yields:

$$U_{\tilde{n},\check{n}}(t_1,t_2) = \varphi \; < \tilde{n} \left| \, e^{iv\tilde{b}^+} |\hat{U}| e^{iu\check{b}} \, \right| \check{n} > \quad , \tag{4.24}$$

$$\begin{aligned} u &= \frac{1}{\sqrt{2\bar{A}}} \left[\tilde{\gamma} t_1 - \check{\gamma}(\bar{B} - \bar{A}) t_2\right] \quad , \\ v &= \frac{1}{\sqrt{2\bar{A}}} \left[\tilde{\gamma}(\bar{A} + B) t_1 + \check{\gamma} t_2\right] \quad . \end{aligned} \tag{4.25}$$

Applying the exponential operators in Eq.(4.24) to the left and right, one finally obtains the result

$$\begin{aligned} U_{\tilde{n},\check{n}}(t_1,t_2) &= \varphi \sum_{s=0}^{\tilde{n}} \sum_{r=0}^{\check{n}} \frac{v^s u^r}{s!r!} \, i^{s+r} \sqrt{\frac{\tilde{n}!\check{n}!}{(\tilde{n}-s)!(\check{n}-r)!}} \, U_{\tilde{n}-s,\check{n}-r} = \\ &= e^{-\frac{\tilde{\gamma}^2}{4}\left(1+\frac{B}{\bar{A}}\right)t_1^2 - \frac{\check{\gamma}^2}{4}\left(1-\frac{\bar{B}}{\bar{A}}\right)t_2^2} \, e^{i\tilde{\gamma}\left(\tilde{\Delta}-\frac{\check{G}}{\sqrt{2\bar{A}}}\right)t_1} \, e^{i\check{\gamma}\left(\check{\Delta}-\frac{\bar{G}}{\sqrt{2\bar{A}}}\right)t_2} \\ &\quad \times \; e^{\frac{-\tilde{\gamma}\check{\gamma}}{2\bar{A}} t_1 t_2} \sum_{s=0}^{\tilde{n}} \sum_{r=0}^{\check{n}} \frac{i^{s+r}}{s!r!} \sqrt{\frac{\tilde{n}!\check{n}!}{(\tilde{n}-s)!(\check{n}-r)!}} \\ &\quad \times v^s u^r \, U_{\tilde{n}-s,\check{n}-r} \quad . \end{aligned} \tag{4.26}$$

The terms $U_{\tilde{n}-s,\check{n}-r}$ are derived in Appendix B, while the double integration is performed in Appendix C of Ref.[46]

B) Case of no nuclear potential crossing

For the case where, for example, the nuclear potentials $E_i(\tilde{\omega},\tilde{Q})$ and $E_j(\check{\omega},\check{Q})$ do not cross $E_f(\omega,Q)$, it follows from Eqs.(3.12) and (4.7) that

$$\begin{aligned} &< \tilde{n} \left| \, e^{i\tilde{p}\tilde{\Delta}} \, \frac{1}{\tilde{\xi}^+} \, e^{\hat{H}_f \, \tau/\hbar} \, \frac{1}{\check{\xi}} \, e^{-i\check{p}\check{\Delta}} \, \right| \check{n} > = \\ &\left(\frac{\tilde{\delta}\check{\delta}}{4\tilde{\omega}\tilde{\kappa}\check{\omega}\check{\kappa}} \right) \\ &\times \int_0^\infty dt_1 \int_0^\infty dt_2 \left[W'(t_1,t_2) + W'(t_1,-t_2) + W'(-t_1,t_2) + W'(-t_1,-t_2)\right] \\ &\qquad \times e^{-\tilde{\kappa}t_1 - \check{\kappa}t_2} \quad , \end{aligned} \tag{4.27}$$

$$W'(x,y) = e^{-i(\tilde{\gamma}/2-\tilde{\delta}\tilde{\Delta})x} \, e^{-i(\check{\gamma}/2-\check{\delta}\check{\Delta})y} \, \bar{W}'(x,y,\tilde{\delta},\check{\delta}) \quad , \tag{4.28}$$

where $\bar{W}'(x, y, \tilde{\delta}, \check{\delta})$ means evaluating $\bar{W}(x, y)$ of Eq.(4.12) when $\tilde{\gamma}, \check{\gamma}$ is replaced by $\tilde{\delta}, \check{\delta}$.

C) Mixed case

It is assumed, for example, that $E_j(\check{\omega}, \check{Q})$ crosses $E_f(\omega, Q)$ while $E_i(\tilde{\omega}, \tilde{Q})$ does not. For this model one thus obtains

$$< \tilde{n} \left| e^{i\tilde{p}\tilde{\Delta}} \frac{1}{\tilde{\xi}+} e^{\hat{H}_f \tau/\hbar} \frac{1}{\check{\xi}} e^{-i\check{p}\check{\Delta}} \right| \check{n} >= N_1 \left[W(\tilde{Q}_1) - W(\tilde{Q}_2) \right] ,$$
$$N_1 = \frac{\tilde{\gamma}\check{\delta}}{4\tilde{\omega}\check{\kappa}\sqrt{\tilde{\gamma}^2 - \frac{4\tilde{\delta}\tilde{\Delta}E'}{\tilde{\omega}}}} , \tag{4.29}$$

where

$$W(\tilde{Q}_\sigma) = N_1 \int_0^\infty dt_1 \int_0^\infty dt_2 \left[W'(\tilde{Q}_\sigma, t_1, t_2) - W'(\tilde{Q}_\sigma, -t_1, t_2) + W'(\tilde{Q}_\sigma, t_1, -t_2) + W'(\tilde{Q}_\sigma, -t_1, -t_2) \right] \tag{4.30}$$

and

$$W'(\tilde{Q}_\sigma, t_1, t_2) = e^{-i\tilde{\gamma}(\tilde{Q}_\sigma - \tilde{\Delta})t_1} e^{-\check{\kappa}t_2} \times e^{-i(\check{\gamma}/2 - \check{\delta}\Delta)t_2} \bar{W}'(t_1, t_2, \tilde{\gamma}, \check{\delta}) , \tag{4.31}$$

where $\bar{W}'(t_1, t_2, \tilde{\gamma}, \check{\delta})$ means evaluationg $\bar{W}(x, y)$ of Eq.(4.12) when $\check{\gamma}$ is replaced by $\check{\delta}$.

V. Results

As a first point the problem of crossed potential surfaces is investigated for the ν_2 modes of benzene and deuterobenzene. There then follows an investigation of the statistical weights of matrix elements and their various influences on the rates in the Condon and non-Condon schemes. Finally, for benzene and deuterobenzene calculations of the non-Condon rates for a two-electronic-level system are presented as a supplement to Ref.[46]. Rates following from the Condon approximation case are compared with results obtained when the matrix elements of certain modes are replaced by the relevant non-Condon terms.

A) Crossing points of the ν_2 vibration

To obtain an expression accessible to calculations, one introduces the following approximations for Eqs. (2.13-2.15) . For vibrations with higher wave numbers in the upper electronic state, especially the "promoting" mode ν_{14} and the CH-stretch mode ν_2, the square root is expanded in normal coordinates up to second order. If one calculates the one-dimensional non-Condon problem for modes where the upper frequencies are lower than those of the ground state (especially the ν_4), the coupling term $< \varphi_f^0 \left|\bar{U}\right| \varphi_i^0 >$ is neglected because it is very small in the case of benzene. In both cases all the remaining modes are neglected as in hitherto known investigations. However, if one mode accepts a considerable amount of the energy, this approximation will break down since the zeros in the square root expression of Eq.(2.15) play a decisive part, and a still more elaborate formalism should be introduced[38,41,42,83-85]. There are, however, many ways of avoiding the crossing points of a harmonic concept, e.g. Morse oscillator potentials, the local mode picture or strong coupling effects at higher occupation numbers, which lead to a breakdown of the single vibration harmonic mode concept. Strong coupling effects in Eq.(2.15) , at least between the ν_2, ν_4 and the promoting mode ν_{14} , should therefore be expected, these resulting in probably strong, non-harmonic wave equations. In addition, if the S_1 state frequency is lower than that for the S_0, this being identical with the condition for crossing points, as is the case for the ν_4 vibration, the decoupling problem leading to separate eigenvalue problems for the vibrations in the S_1 and S_0 electronic states has to be re-examined[21,38,39,81].

A $S_1 \rightsquigarrow S_0$ rate calculation for benzene with a harmonic basis set shows a nascent energy redistribution in S_0 where no mode receives more than 20% of the energy. The approximations so far are therefore expected to be of the necessary quality. However, it should be mentioned that this may no longer be the case if one introduces the Morse oscillator potentials in the ν_1 and/or ν_2 mode for single vibronic level excitations or for communicating states rate calculations. In the latter, at higher excess energies about 80% of the energy is accepted by the ν_4 out-of-plane mode, which has the lowest potential crossing points of all modes. In benzene many authors have, for example, introduced non-diagonal terms in the kinetic energy operator (local modes)[2,86-89] or nondiagonal terms in the potential energy operator[79] and anharmonic diagonal potentials[52,79]. Effects of the crossing points are therefore widely artificial mathematical effects existing only in a non-Condon scheme of harmonic basis sets . When the rates are calculated with a generating function formalism, matrix elements with very high occupation numbers are used quite far above the crossing points. However, with complete basis sets their influence is obviously extremely damped. One may generally suppose that the local mode idea also in the case of all out-of-plane modes is such an example. The local mode picture of the CH-stretch modes impressively demonstrates this situation.

The problem of crossing points in the energy denominator should now be investigated more closely. Many authors have argued that crossings of the hypersurfaces are mainly responsible for a huge non-Condon effect and nonradiative rate increase, and in the case of benzene especially those along the CH-stretch mode ν_2

and the promoting modes are of decisive importance[7,8]. However, for the known parameters along these modes no crossings occur at all in benzene. This is obvious for the ν_{14} vibration, where the S_1 frequency $\omega_{14}^{S_1} = 1563\ cm^{-1}$ is much higher than that of the ground state $\omega_{14}^{S_0} = 1310\ cm^{-1}$. The conditions for a crossing of the potential curves of the modes of the S_1 and S_0 states with displacement $\Delta = \tilde{\Delta}$ can be derived from the condition $\Delta E + E_i(\mathbf{Q} - \mathbf{\Delta}) = E_f(\mathbf{Q})$ [7].

As is discussed in Appendix A, no crossing points occur for harmonic and Morse oscillator potentials and the parameters taken from the ν_2 mode in benzene. It might therefore be concluded that for all these models contributions of the crossing points to the non-Condon effect cannot reasonably be expected; so to speak, the experimental parameters known at present for benzene do not suggest such a possibility.

B) Saddle point parameter and statistical weight of the matrix elements

If one starts to calculate the rates, the matrix elements enter the saddle point equations (see Eqs.(3.8)-(3.14)) in a very complex manner. It is thus very difficult to predict whether the matrix elements with high occupation numbers and strong non-Condon factors or the lower ones and weak non-Condon terms dominate the process.

Therefore first of all the non-Condon effect on the matrix elements is demonstrated in Tab.(1). The quotients of non-Condon and Condon matrix elements for transitions from the zeroth initial level to certain final levels $< m|$ is calculated for the ν_1, ν_2 and ν_4 for the $S_1 \rightsquigarrow S_0$ transition in benzene. It is evident that for all modes considered the non-Condon effect increases with higher final occupation numbers. Strong distortions obviously lead to a huge non-Condon effect already for low values of the final occupation numbers, as seen for the ν_4 vibration. The non-Condon factor is considerably higher than for the ν_1 and ν_2 modes. However, for higher final occupation numbers (at comparable resonance energies, e.g. $m_1 \approx 30$, $m_2 \approx 10$ and $m_4 \approx 40$) an almost equally strong effect $\approx 3 - 4 \times 10^2$ is adjusted for all modes, while the increase for the total symmetric modes is demonstrated to be much stronger.

One has to take into account that the saddle point rate equation is generally governed by "non-resonant" matrix elements in contrast to rate equations based on counting algorithms. The small effect of the non-Condon terms on the rates is therefore largely achieved through the different values of the saddle point parameters. These are numerically found from Eq.(3.10). Indeed the values for τ, e.g. at $\Delta E = 38086cm^{-1}$ in the single mode ($\tau_{nC} = 1.310652 \times 10^{-3}$, $\tau_C = 1.511738 \times 10^{-3}$), and complete basis set ($\tau_{nC} = 1.291708 \times 10^{-3}$, $\tau_C = 1.392351 \times 10^{-3}$) calculations are very different. As for both calculations the same non-Condon (Condon) matrix elements enter the calculations, these different τ cause different weighting factors and thus lead to various non-Condon factors. To get an impression of this dependence in Tab.(2), the rates, $Z(\tau)$, $< h(\tau) >$ and $< h^2(\tau) >$ for one mode and complete basis sets in the Condon and non-Condon cases are calculated for different values of the parameter τ . It is obvious from Tab.(2) that after introduction of the non-Condon terms the different variables show a dependence on τ which is orders of magnitude higher in the observed parameter region than in the Condon case.

Whether the "resonance" or "non-resonance" case prevails was considered to be an important question[46]. The answer decides between the "resonance" and "stochastic" type non-Condon effect. The "stochastic" effect leads to a damping of the non-Condon effect caused by the remaining modes ("bath" modes). Therefore in the following for the ν_2 mode the percentage contributions that the square of the matrix elements with different quantum numbers make to the partition function $Z_2(\tau)$, the mean value of the vibrational energy $< h_2(\tau) >$ and the fluctuation of the vibrational energy $< h_2^2(\tau) >$ for the single-mode and complete basis set cases are investigated. Because of the completeness relation relation one has in principle to sum over an infinite final basis set. However, actually the summation can be truncated at finite quantum numbers (here for the ν_2 mode the maximum final quantum numbers is chossen to be $n_{f,max} = 30$) to yield sufficient exact results. The partition function and its first and second derivatives are composed of following terms:

$$\begin{aligned} Z(\tau) &= S_1 \; e^{(\omega_f - \omega_i)\tau/2} \quad , \\ < h(\tau) > &= \frac{S_2}{S_1} + (\omega_i - \omega_f)/2 \quad , \\ < h^2(\tau) > &= \frac{S_3}{S_1} - \left(\frac{S_2}{S_1}\right)^2 \quad , \end{aligned} \tag{5.1}$$

$$\begin{aligned} S_1 &= \sum_{n_f=0}^{n_{f,max}} \left|< n_f|0 >\right|^2 \; e^{n_f \omega_f \tau} \quad , \\ S_2 &= \sum_{n_f=0}^{n_{f,max}} \left|< n_f|0 >\right|^2 n_f \omega_f \; e^{n_f \omega_f \tau} \quad , \\ S_3 &= \sum_{n_f=0}^{n_{f,max}} \left|< n_f|0 >\right| \left(n_f \omega_f\right)^2 \; e^{n_f \omega_f \tau} \quad . \end{aligned} \tag{5.2}$$

The percentage contribution of $S_1(n_f), S_2(n_f)$ and $S_3(n_f)$ to S_1, S_2 and S_3 for the single-mode and complete basis set cases is given in Tab.(3). Obviously the "resonance" matrix elements are of little influence in both cases. Thus in non-Condon rate calculations which employ the saddle-point approximation dominate the large "non-resonance" matrix elements. Only about 5% is contributed to the three variables $Z(\tau), < h(\tau) >$ and $< h^2(\tau) >$ from matrix elements lying in the energy range defined by $\epsilon_f = \epsilon_i \pm 9000 cm^{-1}$. $Z(\tau)$ consists to more than 50% of contributions from matrix elements with quantum numbers < 5.

As a consequence the small non-Condon effect obtained with complete basis sets are mainly due to the stochastic redistribution of the energy induced by the "bath" modes. This has also important consequences for the remaining non-Condon theories. As in these theories the non-Condon matrix elements are often lower than those obtained in this work the non-Condon effect must be similarly damped if complete basis sets are employed.

C) Calculation of non-radiative rates

A more detailed discussion of the rate calculation is given in Ref.[46]. While that publication only presents a few examples of special modes, supplementary calculations are given here. While one can find as a gross feature a non-Condon effect which is less than a factor ≈ 3 for all calculations with highly different examples, the fine structure shows essential deviations with respect to the special mode treated within a non-Condon scheme.

a) Influence of energy gap variation on the rate

In Tab.(4) one-mode rate calculations are investigated. The rate is given as a function of the $S_1 \rightsquigarrow S_0$ energy gap. Data for the modes are taken from the ν_2 and ν_4 of C_6H_6 . The result for the ν_2 mode in benzene is found to be identical to that given by Nitzan and Jortner[7] when equal frequencies in the initial and final states are assumed.

In Tab.(5) and (6) the corresponding result for the ν_2 vibration is given when a complete basis set is used. Additionally, the energy redistribution for the main acceptors was investigated. Modes which accept fewer than 2% of the total energy are omitted in the Tables (Tables (5) - (16)). First of all the drastic decline of the non-Condon effect on the quotients of the rates is eminent when compared with the single-mode result. At the benzene $S_1 \rightsquigarrow S_0$ energy gap one finds just a factor ≈ 1.5 instead of ≈ 518 . A still smaller factor is found for deuterobenzene in Tab.(6) . Although in C_6H_6 and C_6D_6 the frequencies and also their relative sizes with respect to all other modes are very different, the non-Condon correcton factor is less than ≈ 2. It is noteworthy that the slopes of the non-Condon factors with the energy gap for the two molecules are exactly the reverse of one another.

One should also compare the energy acceptor behaviour with the results of the Condon approximation. For deuterobenzene at high energy gaps only a small energy redistribution of $< 2\%$ occurs while at low energy gaps the difference is higher than 10% (see Ref.[90]). Because of the very high frequencies of the ν_2 mode in benzene the redistribution on introducing the non-Condon matrix elements is more spectacular. At high energy gaps more than thrice the energy ($\approx 50\%$) is accepted, and twice at low energy gaps ($\approx 40\%$). This energy largely stems from the other CH stretch vibrations (ν_{13}, ν_{20}) and the CC stretch mode ν_1. Although this highly different behaviour for benzene and deuterobenzene would suggest a similarly different effect on the rates, this is obviously not found. For non- Condon calculations energy redistribution seems to be less important on the rate than for problems including anharmonicities.

The variations of the non-Condon factors for C_6D_6 and C_6H_6 are compared in Tab.(7) for the ν_1, ν_4 and ν_{14}. The calculations are generally very cumbersome and in many cases the calculations diverge[91] (indicated by dashes in Table (7)). However, it is clearly shown that in a reasonable energy region where the actual molecular parameters correspond to the weak coupling case the non-Condon effect is very small with the exception of the ν_{14} mode in C_6D_6. This very different influence of the ν_{14} mode seems to underline the necessity of investigating the non-Condon coupling of the ν_2 and the ν_{14} modes, especially since the ν_{14} acts as the promoting mode for the nonradiative decay[92].

b) Rates from single vibronic levels

The rates for progressions of the ν_4 vibration of benzene are calculated in Table (8). As was already shown for the remaining modes treated in Ref.[46], it is also found for the ν_4 modes that the introduction of the non-Condon terms exerts, in contrast to the expected results, a very small increase of the rates even from high initial occupation numbers.

In deuterobenzene the frequencies are very different to those in benzene. Especially the promoting mode ν_{14} has a dominant influence. The increase of the non-Condon rates is investigated in Tabs.(9)-(12) for the ν_1 (Tab.(9)), ν_2 (Tab.(10)), ν_4 (Tab.(11)) and ν_{14} (Tab.(12)). Here again one finds only a very small increase of the rates ($<\approx 4$), even from high progressions of the ν_1, ν_4 modes and also for the ν_2 CH-stretch vibration. Surprisingly, this is also true of the ν_{14} (Tab.(12)). However, for low initial progressions a huge amount of the total energy is redistributed in the ν_{14} and ν_4 cases on introducing the non-Condon terms. The summary of the results in Tabs.(9)-(12) provides confirmation that also for deuterobenzene only a very small non-Condon effect (generally smaller than for benzene) is realized.

It should be mentioned that one can obviously observe a different behaviour of the rate increase with higher progressions for the total symmetric modes, on the one hand, and the out-of-plane modes ν_4 and the promoting mode ν_{14}, on the other. While the first show a continuing increase with higher progressions, the others obviously assume a maximum non-Condon effect.

c) Rates applying the communicating states concept

Our recent calculations[49,50] based on the communicating states model[47,48] seemed to describe many details of the experimental results. It is therefore of some interest to demonstrate the effect of the non-Condon terms especially for this model. In Tab.(13) the rates are calculated as a function of the excess energies in benzene with non-Condon terms in the ν_2 (Tab.(13)), complete basis set) . The results for deuterobenzene are presented in Tab.(14) for the ν_1, Tab.(15) for the ν_2,and Tab.(16) for the ν_4 vibrations. The corresponding energy redistributions in the S_0 state for the Condon approximation case have already been given elsewhere[49,52].

As already mentioned and discussed, the non-Condon rates, calculated here, are in agreement with the results in Ref.[46]. Especially the rate behaviour for the ν_4 mode in deuterobenzene is qualitatively identical to that in benzene.

However, the "fine structure" distinctly shows a remarkable difference when one focuses on the variation of the non-Condon effect with varying excess energy.

In C_6D_6 rate calculations with ν_{14} mode non-Condon terms, the non-Condon factor decreases within $\approx 300cm^{-1}$ from a factor ≈ 1.4 to ≈ 0.65. At the same time the energy acceptance decreases from 37% to 6%, whereas for the ν_4 mode the energy acceptance is increased from 6% to 48%. At higher excess energies the non-Condon effect then seems to be almost constant.

The maximum of the ν_4 mode non-Condon factor seems to be due to the increasing energy acceptance of the out-of-plane mode ν_{16}. Calculated from the maximum excess energy to $6300cm^{-1}$ its acceptance increases by a factor ≈ 4 in benzene and deuterobenzene (Tab.(4) of Ref.[46] and Tab.(16)). The non-Condon factor for both molecules shows the steepest decent for this mode. The non-Condon factor assumes at an excess energy of $6300cm^{-1}$ $\approx 1/10$ of the value found at the maxima although the energy acceptance hardly changes.

For the rate with ν_2 non-Condon matrix elements the non-Condon factor is constant for energies higher than $\approx 1700cm^{-1}$. In relation to the factor obtained at zero excess energy one finds a decrease in C_6H_6 by about a factor four and in C_6D_6 by ≈ 1.6.

The smoothest decrease is shown for the ν_1 modes. For both molecules the non-Condon factor assumes $\approx 1/2$ at an excess energy of $6300cm^{-1}$.

Although the frequencies of the modes are very different in C_6H_6 and C_6D_6, the variation of the non-Condon factor with the excess energy is very similar in both molecules for the actual modes treated within the non-Condon scheme. However, the non-Condon factor shows highly different excess energy behaviour for the various modes. It is obvious that the ν_4 mode with its enormous increase of energy acceptance (about a factor 12) plays an important role for the explanation of the excess energy behaviour. Nevertheless this explanation does not account for the arbitrary deviations. This question has therefore to be left unanswered.

A résumé of all calculations performed within a two-electronic-level model allows one to conclude that the non-Condon treatment in no case yields an increase or change of rates that would be comparable to, for example, those effects caused by the introduction of Morse oscillators or local modes. Obviously, the "bath" modes suppress the effects shown in an one-mode calculation.

D) Three-electronic-state model

Non-radiative rates in a three-electronic-state model were recently calculated[57]. In an approximative model where the excited states are coupled by a non-totally symmetric mode, the rate is calculated as a function of the energy gap, coupling constant and distortion of the coupling mode. As in the work of Penner et al.[37,55] a considerable effect, which is dependent on the various parameters chosen, is found. Especially rates from higher vibronic levels of the S_1 show an increase of the rates by more than two orders of magnitude.

The most interesting model would be to calculate rates according to the communicating states model or the single vibronic concept when the second excited state (A_{2u}) is coupled by the out-of-plane mode ν_4 to the $S_1(B_{2u})$ state. This investigation is being prepared in a forthcoming paper[78].

The three-electronic-state model is especially applicable for those aromatic molecules which show radiative decay of excited electronic-vibrational states in the vicinity of the S_2 configuration[90], e.g. azulene .

Conclusions

An exact and approximative three-level model for the non-radiative transition is deduced. Generating functions for the non-Condon scheme are developed. The formalism also includes the case where the initial states are a mixture of vibronic states which belong to different electronic states. The treatment includes potential crossing and non-crossing cases.

Furthermore, for the special case of benzene and deuterobenzene the question of potential crossings is investigated. It is found that neither for a harmonic potential model nor for a Morse oscillator shape of the potential and/or a local mode concept of the ν_2 mode potential crossings seem to be decisive for non-radiative decay from the S_1 state.

In addition supplementary calculations of non-radiative rates from the S_1 in a two-level model are presented. The various slopes of the non-Condon factors with the excess energy are discussed on the basis of the communicating states model.

Finally, the dependence of the rate equation on the saddle-point parameter was investigated for the Condon and non-Condon cases.

Appendix A

In the case of one-dimensional potential surfaces the condition for crossing of the potential curves of the ν_2 mode is of the form

$$\frac{\omega_i}{2}(Q_2-\Delta)^2+\Delta E=\frac{\omega_i}{2}\,\frac{\omega_f^2}{\omega_i^2}\,Q_2^2 \ , \qquad (A1)$$

where the values for the ν_2 mode have to be inserted[93] ($\omega_2^{S_1}=3130\ cm^{-1}$,$\omega_2^{S_0}=3073\ cm^{-1}$, $\Delta=0.331$ Å, $\Delta E_{S_1,S_0}=38086\ cm^{-1}$) . From Eq.(A1) the crossing points are found to be

$$Q_{1,2}=\frac{1}{2\delta}\left[\Delta\pm\left(\Delta^2-4\delta\frac{\Delta E'}{\omega_i}\right)^{\frac{1}{2}}\right] \ ,$$
$$\delta=\frac{1}{2}\left(1-\frac{\omega_f^2}{\omega_i^2}\right) \ , \qquad (A2)$$

If in Eq.(A2) the root is non-negative, one obtains

$$\Delta^2-4\delta\frac{\Delta E'}{\omega_i}>0 \ . \qquad (A3)$$

This leads to the following condition :

$$\Delta^2>2\left(\frac{\omega_i^2}{\omega_f^2}-1\right)\frac{\Delta E^0_{S_1,S_0}}{\omega_i} \ . \qquad (A4)$$

Inserting the values given above, one obtains $\Delta>0.9545$ Å. The actual value, however, is $\Delta=0.331$ Å. No crossings can thus occur for the harmonic ν_2 vibration. Many publications extend their treatment of the rate calculation by assuming a Morse potential for the ν_2 normal mode or for the CH-stretch local modes. The introduction of this form of anharmonicity has the advantage of better agreement with experimental results and causes at the same time the ν_2 mode to become the main acceptor mode in numerical calculations. Köppel et al. argued that the crossing of the totally symmetric modes is responsible for dramatic nonadiabatic effects[69,70,85] . Crossing points of the energy denominator are therefore also investigated in the following for Morse oscillator potentials of the vibrations. These crossing points can be found by the equation ($\alpha_i=\alpha_f$)

$$D_i\left[1-e^{-\alpha(q-q_0^i)}\right]^2+\Delta E=D_f\left[1-e^{-\alpha(q-q_0^f)}\right]^2 \ , \qquad (A5)$$

where the anharmonicity constants α and κ are assumed to be identical in the S_1 and S_0 electronic states[94], respectively. In the upper electronic state these anharmonic constants are largely unknown but are supposed to be higher than those for the ground state. This leads to the identity $D_i = \frac{\omega_i^2}{\omega_f^2} D_f$. Solving Eq.(A5) for q, one obtains

$$\Delta E < \frac{\omega_f^2}{4\kappa} \frac{1 + e^{2\alpha\Delta q} - 2e^{\alpha\Delta q}}{e^{2\alpha\Delta q} - \frac{\omega_f^2}{\omega_i^2}} \tag{A6}$$

and

$$\frac{\omega_f^2}{\omega_i^2} - e^{2\alpha\Delta q} \qquad > 0 \ . \tag{A7}$$

When the actual values[95] $\kappa = 9.2\ cm^{-1}$ and $\Delta q = -0.028$ Å are inserted in Eq.(A6), the crossing point occurs at $\Delta E > 2285365\ cm^{-1}$, about nine times higher than the experimental dissociation limit D_f . For the Morse oscillator model, potential crossing thus occurs, but far above the dissociation limits of both electronic states. It therefore seems rather justified to neglect the contributions of the crossing points to the values of the matrix elements within bound states. For the local mode picture with the parameters[95] $\omega_f = 3273\ cm^{-1}, \omega_i = 3183\ cm^{-1}, \Delta q = -0.01143$ Å and $\kappa = 55.2\ cm^{-1}$ crossing points would only occur at energy gaps lower than $\Delta E < 1200\ cm^{-1}$.

Appendix B

$$
\begin{aligned}
A &= \tilde{\alpha}\check{\alpha}\ e^{i\omega t} - \tilde{\beta}\check{\beta}\ e^{-i\omega t} \quad , \\
B &= \tilde{\alpha}\check{\beta}\ e^{i\omega t} - \check{\alpha}\tilde{\beta}\ e^{-i\omega t} \quad , \\
\check{B} &= \check{\alpha}\tilde{\beta}\ e^{i\omega t} - \check{\beta}\tilde{\alpha}\ e^{-i\omega t} \quad , \\
G &= \frac{\tilde{\Delta}}{\sqrt{2}} - (\check{\alpha} + \check{\beta})(\tilde{\alpha}e^{i\omega t} - \tilde{\beta}e^{-i\omega t})\ \frac{\check{\Delta}}{\sqrt{2}} \quad , \\
\check{G} &= \frac{\check{\Delta}}{\sqrt{2}} - (\tilde{\alpha} + \tilde{\beta})(\check{\alpha}e^{i\omega t} - \check{\beta}e^{-i\omega t})\ \frac{\tilde{\Delta}}{\sqrt{2}} \quad .
\end{aligned}
\tag{B1}
$$

Variables in Eqs.(B1) which carry a bar in the text mean the conjugate complex values.

The generating function $U_{\tilde{n},\check{n}}(it)$ for harmonic vibrations is explicitly derived in Ref.[77]:

$$
\begin{aligned}
U_{\tilde{n},\check{n}} &= < \tilde{n} \left| \ e^{i\tilde{p}\tilde{\Delta}}\ e^{i\omega b^{+}bt}\ e^{-i\check{p}\check{\Delta}} \ \right| \check{n} >= \\
& U_{0,0}\sqrt{\tilde{n}!\ \check{n}!}\ \sum_{k=0}^{[\tilde{n},\check{n}]} \frac{R_{\tilde{n}-k}(x_1,y_1)\ R_{\check{n}-k}(x_2,y_2)}{k!\ \bar{A}^k} \quad ,
\end{aligned}
\tag{B2}
$$

$$
x_1 = \frac{B}{2\bar{A}} \quad , \qquad y_1 = -\frac{\check{G}}{\bar{A}} \quad ,
$$

$$
x_2 = \frac{\check{B}}{2\bar{A}} \quad , \qquad y_2 = -\frac{\bar{G}}{\bar{A}} \quad , \tag{B3}
$$

$$
U_{0,0} = \frac{1}{\sqrt{\bar{A}\ e^{i\omega t}}}\ exp\left[-\frac{\check{\Delta}\bar{G} + \tilde{\Delta}\check{G}}{2\sqrt{2}\bar{A}} \right] \quad , \tag{B4}
$$

$$
R_1(x,y) = 0 \quad , \qquad R_0(x,y) = 1 \quad ,
$$

$$
R_l(x,y) = \left[2xR_{l-2}(x,y) + yR_{l-1}(x,y)\right]/l \quad . \tag{B5}
$$

The partial derivatives of $\bar{W}(t_1,t_2) = \bar{W}_{\tilde{n},\check{n}}(t_1,t_2)$ with respect to τ $(\tau = -it)$ yield $(\bar{W}_{\tilde{n},\check{n}} = \bar{W}_{\tilde{n},\check{n}}(t_1,t_2))$

$$\begin{aligned}\frac{1}{\omega}\ \frac{\partial \bar{W}_{\tilde{n},\check{n}}}{\partial\tau} =& A_1\sqrt{(\check{n}+1)(\check{n}+2)}\ \bar{W}_{\tilde{n},\check{n}+2} + A_3\sqrt{\check{n}+1}\ \bar{W}_{\tilde{n},\check{n}+1} \\ &+ (A_4\check{n} + A_5)\ \bar{W}_{\tilde{n},\check{n}} + A_2\sqrt{\check{n}}\ \bar{W}_{\tilde{n},\check{n}-1} \\ &+ A_1\ \sqrt{\check{n}(\check{n}-1)}\ \bar{W}_{\tilde{n},\check{n}-2}\ ,\end{aligned} \tag{B6}$$

$$\begin{aligned}\frac{1}{\omega^2}\ \frac{\partial^2 \bar{W}_{\tilde{n},\check{n}}}{\partial\tau^2} =& A_1^2\sqrt{(\check{n}+1)(\check{n}+2)(\check{n}+3)(\check{n}+4)}\ \bar{W}_{\tilde{n},\check{n}+4} \\ &- 2A_1A_2\sqrt{(\check{n}+1)(\check{n}+2)(\check{n}+3)}\ \bar{W}_{\tilde{n},\check{n}+3} \\ &+ \sqrt{(\check{n}+1)(\check{n}+2)}\ [A_2^2 + 2A_5A_1 + 2A_1A_4(\check{n}+1)]\bar{W}_{\tilde{n},\check{n}+2} \\ &\sqrt{\check{n}+1}\ [-A_2A_4(2\check{n}+1) + 2A_1A_3(\check{n}+1) - 2A_5A_2]\ \bar{W}_{\tilde{n},\check{n}+1} \\ &+ [(A_4^2 + 2A_1^2)\check{n}\check{n} + 2(A_5A_4 - A_2A_3 + A_1^2)\check{n} + A_5^2 \\ &- A_2A_3 + 2A_1^2]\ \bar{W}_{\tilde{n},\check{n}} \\ &+ \sqrt{\check{n}}\ [A_3A_4(2\check{n}-1) - 2\check{n}A_1A_2 + 2A_5A_3]\ \bar{W}_{\tilde{n},\check{n}-1} \\ &+ \sqrt{\check{n}(\check{n}-1)}\ [A_3^2 + 2A_5A_1 + 2A_1A_4(\check{n}-1)]\ \bar{W}_{\tilde{n},\check{n}-2} \\ &+ \sqrt{\check{n}(\check{n}-1)(\check{n}-2)}\ 2A_1A_3\ \ \bar{W}_{\tilde{n},\check{n}-3} \\ &+ A_1^2\sqrt{\check{n}(\check{n}-1)(\check{n}-2)(\check{n}-3)}\ \ \bar{W}_{\tilde{n},\check{n}-4}\ .\end{aligned} \tag{B7}$$

$$\begin{aligned}A_1 =& \check{\alpha}\check{\beta}\ , \\ A_2 =& \frac{\check{\Delta}}{\sqrt{2}}\ (\check{\alpha}+\check{\beta})^2 - \frac{i\check{\gamma}}{\sqrt{2}}t_2(\check{\alpha}-\check{\beta})^2\ , \\ A_3 =& +\ \frac{\check{\Delta}}{\sqrt{2}}\ (\check{\alpha}+\check{\beta})^2 + \frac{i\check{\gamma}}{\sqrt{2}}t_2(\check{\alpha}-\check{\beta})^2\ , \\ A_4 =& \check{\alpha}^2 + \check{\beta}^2\ , \\ A_5 =& \frac{\check{\Delta}^2}{2}\ (\check{\alpha}+\check{\beta})^2 + \check{\beta}^2 + \frac{\check{\gamma}^2}{2}\ t_2^2\ (\check{\alpha}-\check{\beta})^2\ .\end{aligned} \tag{B8}$$

Appendix C

The terms in Eq.(4.26) lead to the following integrals:

$$I(t_1,t_2) = \int_0^\infty dt_1 \int_0^\infty dt_2 \; e^{-D_1 t_1^2 - D_2 t_2^2} \; e^{-iE_1 t_1} \times e^{-iE_2 t_2} \; e^{-F t_1 t_2} \; t_1^l t_2^k \; , \tag{C1}$$

$$\begin{aligned} D_1 &= \frac{\tilde{\gamma}^2}{2}\left(1 + \frac{B}{\bar{A}}\right) \; , \\ D_2 &= \frac{\check{\gamma}^2}{2}\left(1 - \frac{\bar{B}}{\bar{A}}\right) \; , \\ E_1 &= i\tilde{\gamma}\left(\tilde{\Delta} - \frac{\check{\tilde{G}}}{\sqrt{2\bar{A}}}\right) + E_{11} \; , \\ E_2 &= i\check{\gamma}\left(\check{\Delta} - \frac{\tilde{G}}{\sqrt{2\bar{A}}}\right) + E_{22} \; , \\ F &= \frac{\tilde{\gamma}\check{\gamma}}{2\bar{A}} \; . \end{aligned} \tag{C2}$$

a) For the crossing case of the nuclear potentials (Eq(4.11)) one obtains:

$$E_{11} = -i\tilde{\gamma}(\tilde{Q}_\sigma - \tilde{\Delta}) \; , \quad E_{22} = \check{\gamma}(\check{Q}_{\sigma'} - \check{\Delta}) \; , \tag{C3}$$

b) Case of no nuclear potential crossings (Eq.(4.28)):

$$E_{11} = -i\left(\frac{\tilde{\gamma}}{2} - \tilde{\delta}\tilde{\Delta}\right) \; , \quad E_{22} = -i\left(\frac{\check{\gamma}}{2} - \check{\delta}\check{\Delta}\right) \; , \tag{C4}$$

c) Mixed case (Eq.(4.31)):

$$E_{11} = -i\tilde{\gamma}(\tilde{Q}_\sigma - \tilde{\Delta}) \; , \quad E_{22} = -\check{\kappa} - i(\check{\gamma}/2 - \check{\delta}\check{\Delta}) \; , \tag{C5}$$

d) In the limit of a two level model one finds

$$D_1 = D_2 \quad , \tag{C6}$$

$$E_1 = E + \gamma \tilde{Q}_\sigma - \gamma \tilde{\Delta} \quad , \qquad E_2 = E + \gamma \tilde{Q}_{\sigma'} - \gamma \tilde{\Delta} \quad , \tag{C7}$$

for the potential crossing case, and

$$E_1 = E_2 = E + \gamma/2 - \delta \tilde{\Delta} + i\kappa \quad , \tag{C8}$$

for the non-crossing case.

In the limit of the two electronic state model one gets the corresponding expressions to the integrals in Eq.(4.26) and the partial derivatives of $\bar{W}_{\tilde{n},\tilde{n}'}$ (Eq.(C2) of Ref.[46], Eqs.(B6) and (B7) of Appendix B) if in all terms $\breve{n}$ is replaced by $\tilde{n}'$ and in all variables the hook is replaced by the tilde.

Appendix D

Finally one has to evaluate the double integration procedure in Eq.(C1).

$$I(t_1, t_2) = i^{l+k} \left(\frac{\partial}{\partial E_1} \right)^l \left(\frac{\partial}{\partial E_2} \right)^k I_0(t_1, t_2) \quad , \tag{D1}$$

$$I_0(t_1, t_2) = \int_0^\infty dt_1 \int_0^\infty dt_2 \; e^{-D_1 t_1^2 + D_2 t_2^2 - iE_1 t_1 - iE_2 t_2 - F t_1 t_2} \quad , \tag{D2}$$

Performing the integration with respect to t_1 yields

$$I_0(t_2) = \sqrt{\frac{\pi}{4D_1}} \; exp \frac{(Ft_2 + iE_1)^2}{4D_1} \; erfc \left(\frac{Ft_2 + iE_1}{2\sqrt{D_1}} \right) \quad . \tag{D3}$$

Hence, for the t_2 integration one gets the expression

$$I_0(t_1, t_2) = \sqrt{\frac{\pi}{4D_1}} \; [I_{t_2}^1 - I_{t_2}^2] \quad , \tag{D4}$$

where

$$I_{t_2}^1 = \int_0^{\infty} e^{-D_2 t_2^2 - iE_2 t_2} \; exp\left[\frac{(Ft_2 + iE_1)^2}{4D_1}\right] dt_2 =$$

$$\sqrt{\frac{\pi D_1}{4D_1D_2 - F^2}} \; erfc\left[\frac{\sqrt{D_1}}{F} \frac{E_2F - 2E_1D_2}{\sqrt{F^2 - 4D_1D_2}}\right] \tag{D5}$$

$$\times \; exp\left[-\frac{D_2E_1^2 + D_1E_2^2 - FE_1E_2}{4D_1D_2 - F^2}\right] \; ,$$

and

$$I_{t_2}^2 = a_0 \int_{z_0}^{\infty} e^{-a_1 z^2 + i a_2 z} \; erf(z) \; dz \; , \tag{D6}$$

$$z = \frac{Ft_2 + iE_1}{2\sqrt{D_1}} \; ,$$

$$a_0 = \frac{2\sqrt{D_1}}{F} \; exp\left[\frac{D_2E_1^2}{F^2} - \frac{E_1E_2}{F}\right] \; ,$$

$$a_1 = \frac{4D_1D_2}{F^2} - 1 \; , \tag{D7}$$

$$a_2 = \frac{2\sqrt{D_1}}{F^2} \; (2D_2E_1 - E_2F) \; ,$$

$$z_0 = - \, i\frac{E_1}{F} \; .$$

$I_{t_2}^2$ is, to our knowledge, not analytically integrable. Equation (D6) can therefore only be evaluated either by numerical integration or by series expansion methods. Introduction of the series expansion of the complex exponent part in Eq.(D6) leads to

$$I_{t_2}^2(even) = a_0 \sum_{n=0}^{\infty} (-1)^n \frac{a_2^{2n}}{(2n)!} U_{2n} \; ,$$

$$I_{t_2}^2(odd) = i \; a_0 \sum_{n=0}^{\infty} (-1)^n \frac{a_2^{2n+1}}{(2n+1)!} V_{2n+1} \; . \tag{D8}$$

The recurrence relations for the U_{2n} and V_{2n+1} in Eq.(D8) are obtained as follows:

$$U_{2n+2} = \frac{1}{2a_1} \; e^{-a_1 z_0^2} \; erf(z_0) \; z_0^{2n+1} + \frac{1}{2a_1\sqrt{\pi}} \; n! \; e^{-z_0^2} \sum_{k=0}^{n} \frac{z_0^{2k}}{k!} + \frac{2n+1}{2a_1} U_{2n} \; ,$$

$$U_{2n} = \int_{z_0}^{\infty} z^{2n} e^{a_1 z^2} erf(z) \; dz \; , \tag{D9}$$

$$U_0 = \int_{z_0}^{\infty} e^{-a_1 z^2} erf(z)\, dz \quad = \tag{D10}$$
$$\frac{e^{-(1+a_1)z_0^2}}{\sqrt{\pi}(1+a_1)} \sum_{m=0}^{\infty} \frac{(m!)^2 2^{2m}}{(2m+1)!} \frac{1}{(1+a_1)^m} \sum_{k=0}^{m} \frac{1}{k!} \left(\frac{z_0^2}{1+a_1}\right)^k ,$$

$$V_{2n+3} = \frac{2n+2}{2a_1} V_{2n+1} + \frac{1}{2a_1} e^{-a_1 z_0^2} erf(z_0)\, z_0^{2n+2} + \frac{1}{a_1\sqrt{\pi}} W_{2n+2} ,$$

$$V_{2n+1} = \int_{z_0}^{\infty} z^{2n+1} e^{-a_1 z^2} erf(z)\, dz , \tag{D11}$$

$$V_1 = \int_{z_0}^{\infty} z e^{-a_1 z^2} erf(z)\, dz \quad = \tag{D12}$$
$$\frac{1}{2a_1}\left[erf(z_0)\, e^{-a_1 z_0^2} + \frac{1}{\sqrt{1+a_1}} - \frac{1}{\sqrt{1+a_1}} erf(\sqrt{1+a_1}z_0)\right] ,$$

$$W_{2n+2} = \frac{1}{2(1+a_1)} e^{(1+a_1)z_0^2} z_0^{2n+1} + \frac{2n+1}{2(1+a_1)} W_{2n} ,$$

$$W_{2n} = \int_{z_0}^{\infty} z^{2n} e^{-(1+a_1)z^2} dz , \tag{D13}$$

$$W_0 = \frac{1}{2}\sqrt{\frac{\pi}{1+a_1}}\, erfc(\sqrt{1+a_1}z_0) . \tag{D14}$$

Closed-form expressions for the terms in Eq.(D7) are of the form

$$I_{t_2}^2(even) = \frac{a_0}{2(1+a_1)} e^{-(1+a_1)z_0^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} \left(\frac{a_2^2}{1+a_1}\right)^n \tag{D15}$$
$$\times \sum_{m=0}^{\infty} \frac{2^{2m}\, m!\, (m+n)!}{(2m+1)!\, (1+a_1)^m} \sum_{k=0}^{m+n} \frac{\left[(1+a_1)z_0^2\right]^k}{k!} ,$$

$$I_{t_2}^2(odd) = \frac{a_0}{2} \sum_{n=0}^{\infty} (-1)^n \frac{n!}{(2n+1)!} \left(\frac{a_2^2}{a_1}\right)^{n+1} \sum_{k=0}^{\infty} \frac{a_1^k}{k!} \left\{ erf(z_0)\, e^{-a_1 z_0^2} z_0^{2k} + \right.$$
$$\frac{(2k)!}{k!\, 2^{2k}\, (1+a_1)^{k+1/2}} - \frac{2}{\sqrt{\pi}} z_0^{2k+1} \sum_{l=0}^{\infty} \frac{(-1)^l}{l!\, (2l+2k+1)}$$
$$\left. \times \left[z_0^2\, (1+a_1)\right]^l \right\} . \tag{D16}$$

The differentiation with respect to E_1 and E_2 in Eqs.(D3), (D15) and (D16) is easily proved to be straightforward.

REFERENCES

1. S. H. Lin, J. Chem. Phys. **44**, 3759 (1966).
2. W. Siebrand and D. F. Williams, J. Chem. Phys. **49**, 1860 (1968).
3. R. Englman and J. Jornter, Mol. Phys. **18**, 145 (1970).
4. M. G. Prais, D. F. Heller, and K. F. Freed, Chem. Phys. **6**, 331 (1974).
5. K. G. Spears and S. A. Rice, J. Chem. Phys. **55**, 5561 (1971).
6. K. F. Freed and J. Jortner, J. Chem. Phys. **52**, 6272 (1970).
7. A. Nitzan and J. Jortner, J. Chem. Phys. **56**, 3360 (1972).
8. K. F. Freed and S. H. Lin, Chem. Phys. **11**, 409 (1975).
9. Y. Fujimura, H. Kono, and T. Nakajima, J. Chem. Phys. **66**, 199 (1977).
10. O. L. J. Gijzeman, Chem. Phys. Lett. **26**, 152 (1974).
11. J. Brickmann, Chem. Phys. **24**, 367 (1977).
12. G. C. Marconi and G. Orlandi, Chem. Phys. Lett. **21**, 89 (1973).
13. N. Kanamaru and E. C. Lim, Chem. Phys. **10**, 141 (1975).
14. S. F. Fischer, G. L. Hofacker, and R. Seiler, J. Chem. Phys. **51**, 3951 (1969).
15. J. Brickmann and H. Bitto, Chem. Phys. **32**, 143 (1978).
16. B. Sharf and R. Silbey, Chem. Phys. Lett. **9**, 125 (1971) ; ibid. **14**, 315 (1972).
17. W. H. Henneker, W. Siebrand, and M. Z. Zgierski, J. Chem. Phys. **74**, 6560 (1981).
18. B. D. Fainberg, Opt. Spectrosc. (USSR) **51**, 250 (1981).

19. W. Siebrand and M. Z. Zgierski, J. Chem. Phys. **75**, 1230 (1981).

20. W. Siebrand and M. Z. Zgierski, Chem. Phys. Lett. **72**, 411 (1980).

21. H. Köppel, L. S. Cederbaum, and W. Domcke, Chem. Phys. **69**, 175 (1982).

22. M. Jacon, Chem. Phys. Lett. **47**, 466 (1977).

23. C. Otis, J. Knee, and P. Johnson, J. Phys. Chem. **87**, 2232 (1983).

24. J. L. Knee, C. E. Otis, and P. M. Johnson, J. Chem. Phys. **81**, 4455 (1984).

25. C. S. Parmenter and M. W. Schuyler, in Transitions Nonradiative Moleculaire Reunion Soc. Chem. Phys. 20th, 1969, p. 92 (J. Chim. Phys. Suppl. 1969-1970).

26. L. Wunsch, H. J. Neusser, and E. W. Schlag, Z. Naturforsch. **36 A**, 1340 (1981).

27. T. A. Stephenson, P. L. Radloff, and S. A. Rice, J. Chem. Phys. **81**, 1060 (1984).

28. T. A. Stephenson and S. A. Rice, J. Chem. Phys. **81**, 1073 (1984).

29. J. H. Callomon, J. E. Parkin, and R. Lopez-Delgado, Chem. Phys. Lett. **13**, 125 (1972).

30. G. H. Atkinson and C. S. Parmenter, J. Mol. Spectry. **73**, 52 (1978).

31. E. Riedle, H. J. Neusser, and E. W. Schlag, J. Phys. Chem. **86**, 4847 (1982).

32. M. Sumitani, D. V. O'Connor, Y. Takagi, and K. Yoshihara, Chem. Phys. Lett. **108**, 11 (1984).

33. D. V. O'Connor, M. Sumitani, Y. Takagi, N. Nakashima, K. Kamogawa, Y. Udagawa, and K. Yoshihara, J. Phys. Chem. **87**, 4848 (1983).

34. E. Riedle, Thesis, TU München, FRG (1984).

35. M. Jacon, C. Lardeux, R. Lopez-Delgado, and A. Tramer, Chem. Phys. **24**, 145 (1977).

36. W. Siebrand and M. Z. Zgierski, Chem. Phys. Lett. **58**, 8 (1978).

37. A. P. Penner, W. Siebrand, and M. Z. Zgierski, J. Chem. Phys. **69**, 5496 (1978).

38. S. F. Fischer, Chem. Phys. Lett. **91**, 367 (1982).

39. S. F. Fischer and H. Köppel, Chem. Phys. **59**, 279 (1981).

40. N. Heider and S. F. Fischer, Chem. Phys. **88**, 209 (1984).

41. J. S. Alper, J. Chem. Phys. **54**, 3283 (1971).

42. J. S. Alper and R. Silbey, J. Chem. Phys. **52**, 569 (1970).

43. J. H. van Vleck, Phys. Rev. **33**, 467 (1929).

44. A. L. Sobolewski, R. Czerminski, and K. Kuczera, Mol. Phys. **50**, 971 (1983).

45. A. L. Sobolewski and J. Prochorow, Chem. Phys. **92**, 221 (1985).

46. H. Hornburger, Zeitschrift fur Physik D, to be published.

47. S. F. Fischer and E. W. Schlag, Chem. Phys. Lett. **4**, 393 (1969).

48. S. F. Fischer and F. Metz, unpublished results.

49. H. Hornburger, C. M. Sharp, and S. Leach, Chem. Phys. **101**, 67 (1986).

50. H. Hornburger, K.-D. Reinsch, M. Melzig, and S. Leach, Z. Phys. D - Atoms, Molecules and Clusters **5**, 151 (1987).

51. H. Hornburger and J. Brand, Chem. Phys. Lett. **88**, 153 (1982).

52. H. Hornburger, H. Schröder, and J. Brand, J. Chem. Phys. **80**, 3197 (1984).

53. F. Metz, Habilitation, TU München, FRG (1977).

54. D. W. Noid, M. L. Koszykowski and R. A. Marcus, Ann. Rev. Phys. Chem. **32**, 267 (1981).

55. W. H. Henneker, A. P. Penner, W. Siebrand, and M. Z. Zgierski, J. Chem. Phys. **69**, 1884 (1978).

56. W. J. Meath and J. O. Hirschfelder, J. Chem. Phys. **41**, 1628 (1964).

57. H. Hornburger, Thesis, TU München, FRG (1980).

58. R. van Buskirk and C. Jeffries, Phys. Rev. **A 31**, 3332 (1985).

59. J. M. Ziman, Elements of Advanced Quantum Theory, Cambridge, 1969, University Press.

60. P. Roman, Advanced Quantum Theory, Addison and Wesley, Massachusetts, 1965.

61. V. A. Kovarskii, Sov. Phys. Solid State **4**, 1200 (1963) , ibid. **4**, 2345 (1963).

62. G. Amat, Chem. Phys. **71**, 363 (1982).

63. R. V. Jensen and R. Shankar, Phys. Rev. Lett. **54**, 1879 (1985).

64. T. Yukawa, Phys. Rev. Lett. **54**, 1883 (1985).

65. S. A. Rice, Advan. Chem. Phys. **47**, 117 (1981).

66. G. S. Ezra, Chem. Phys. Lett. **101**, 259 (1983).

67. J. Ford and G. H. Lunsford, Phys. Rev. **A 1**, 59 (1970).

68. R. S. Berry, J. Chem. Phys. **78**, 3976 (1983).

69. H. -D. Meyer and H. Köppel, J. Chem. Phys. **81**, 2605 (1984).

70. Th. Zimmermann, H. Köppel, and L. S. Cederbaum, J. Chem. Phys. **83**, 4697 (1985).

71. A. Nitzan, J. Jortner, and B. J. Berne, Mol. Phys. **26**, 281 (1973).

72. A. Nitzan and J. Jortner, J. Chem. Phys. **57**, 2870 (1972).

73. L. Mower, Phys. Rev. **142**, 799 (1966).

74. A. Nitzan and J. Jortner, Mol. Phys. **24**, 109 (1972).

75. Y. Fujimura, N. Shimakura, and T. Nakajima, J. Chem. Phys. **66**, 3530 (1977).

76. W. M. Gelbart and S. A. Rice, J. Chem. Phys. **50**, 4775 (1969).

77. F. Metz, Chem. Phys. **9**, 121 (1975).

78. H. Hornburger et al., in preparation.

79. M. S. Child and L. Halonen, Advan. Chem. Phys. **57**, 1 (1984).

80. A. Chedin and Z. Cihla, J. Mol. Spectrosc. **45**, 475 (1973) ; ibid **49**, 289 (1974).

81. M. E. Kellmann, J. Chem. Phys. **76**, 4528 (1982).

82. M. Abramowitz, I. A. Stegun: Handbook of Mathematical Functions (U. S. GPO, Washington, D. C.,1964).

83. C. A. Mead, J. Chem. Phys. **78**, 807 (1983) ; ibid **70**, 2276 (1979).

84. W. Domcke, H. Köppel, and L. S. Cederbaum, Mol. Phys. **43**, 851 (1981).

85. H. Köppel, H. -D. Meyer, Chem. Phys. Lett. **107**, 149 (1984).

86. J. S. Hutchinson, E. L. Sibert III, and J. T. Hynes, J. Chem. Phys. **81**, 1314 (1984).

87. L. Halonen, Chem. Phys. Lett. **87**, 221 (1982).

88. L. Swofford, M. E. Long, and A. C. Albrecht, J. Chem. Phys. **65**, 179 (1976).

89. P. J. Nagy and W. L. Hase, Chem. Phys. Lett. **54**, 73 (1978).

90. A. Amirav, U. Even, and J. Jornter J. Chem. Phys. **74**, 3745 (1980) and references therein.

91. Throughout the rate calculations one is confronted with two sorts of numerical problems. The first consists in evaluating the matrix elements. The summation of the alternating non-Condon terms requires higher-precision arithmetic if the final occupation numbers are large (we were limited to 32 digits in our computation). However, these limitations can be avoided, in principle, by using the generating function formalism for the wave functions. On the other hand, one is again confronted with the summation of alternating terms or the drastic numerical instabilities of the recurrence relations for many values of the parameters. The second numerical problem evolves from the solution of the saddle-point equation. Enlargement of the non-Condon basis set employed often leads to divergence error. This is most probably due to a limited applicability of the rate calcuations with the saddle-point approximation concept.

92. H. Hornburger, H. Kono, and S. H. Lin, to be published.

93. T. A. Stephenson, Ph.D. Thesis, The University of Chicago, USA (1983).

94. B. I. Makshantsev and I. P. Perstnev, Opt. Spectrosc. **30**, 202 (1971).

95. I. Kühn, D. F. Heller, and W. M. Gelbart, Chem. Phys. **22**, 435 (1977).

Table Captions

Table 1

Quotients of non-Condon and Condon matrix elements $|< m|0>_{nC} / < m|0>_C|$ for certain final occupation numbers m of C_6H_6 ($\Delta E = 38086cm^{-1}$).

Table 2

$z_2(\tau)\,[1.0]$, $Z(\tau)\left[10^{-18}\right]$, $< h_2(\tau) > \left[10^4\right]$, $H(\tau) - \Delta E\left[10^4\right]$, $< h_2^2(\tau) > \left[10^8\right]$ and $< H^2(\tau) > \left[10^8\right]$ as defined in Eqs.(3.8)-(3.14) as functions of the saddle-point parameter τ for all thirty modes (upper case) and for the mode ν_2 in the non-Condon and Condon cases. $*$ and $**$ indicate the solutions for τ_c and τ_{nC}.

Table 3

The percentage contribution which make the matrix elements with final quantum numbers n_f to the partition function $Z(\tau) = S_1$ and its first and second partial derivatives S_2 and S_3 (see Eqs.(5.1) and (5.2)). For the single mode one finds $S_1 = \sum_{n_f=0}^{30} S_1(n_f) = 2.18\times10^{-13}, S_2 = \sum_{n_f=0}^{30} S_2(n_f) = 8.30\times10^{-9}, S_3 =$

$\sum_{n_f=0}^{30} S_3(n_f) = 5.74 \times 10^{-4}, \tau = 1.31064264 \times 10^{-3}$, and similar for the complete basis set: $S_1 = 1.36 \times 10^{-13}, S_2 = 3.07 \times 10^{-9}, S_3 = 1.68 \times 10^{-4}, \tau = 1.29468358 \times 10^{-3}$.

Table 4

Quotients of non-Condon and Condon rates as a function of the $S_1 \rightsquigarrow S_0$ energy gap $[cm^{-1}]$. Single-mode calculations. Data from C_6H_6.

Table 5

Quotients of non-Condon and Condon rates as a function of the $S_1 \rightsquigarrow S_0$ energy gap $[cm^{-1}]$ (Complete basis set of C_6H_6, ν_2 non-Condon terms). Modes which accept fewer than 2% of the total energy are omitted in the Table.

Table 6

Quotients of non-Condon and Condon rates as a function of the $S_1 \rightsquigarrow S_0$ energy gap $\left[cm^{-1}\right]$ (complete basis set C_6D_6, ν_2 non-Condon terms).

Table 7

Quotients of non-Condon and Condon rates as a function of the $S_1 \rightsquigarrow S_0$ energy gap $\left[cm^{-1}\right]$ for complete basis sets in C_6H_6 and C_6D_6 (non-Condon terms are used for the ν_1, ν_2 and ν_{14} each, as specified).

Table 8

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 for ν_4 single vibronic initial levels in benzene (ν_4 non-Condon terms). Modes which accept less than 2% of the total energy are omitted in the table.

Table 9

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 for ν_1 single vibronic initial levels in C_6D_6 (ν_1 non-Condon terms). Modes which accept less than 2% of the total energy are omitted in the table.

Table 10

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 for ν_2 single vibronic initial levels in C_6D_6 (ν_2 non-Condon terms). Modes which accept less than 2% of the total energy are omitted in the table.

Table 11

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 for ν_4 single vibronic initial levels in C_6D_6 (ν_4 non-Condon terms). Modes which accept less than 2% of the total energy are omitted in the table.

Table 12

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 for ν_{14} single vibronic initial levels in C_6D_6 (ν_{14} non-Condon terms). Modes which accept less than 2% of the total energy are omitted in the table.

Table 13

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 in C_6H_6 (ν_2 non-Condon terms, communicating states model). Modes which accept less than 2% of the total energy are omitted in the table.

Table 14

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 in C_6D_6 (ν_1 non-Condon terms, communicating states model).

Modes which accept less than 2% of the total energy are omitted in the table.

Table 15

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 in C_6D_6 (ν_2 non-Condon terms, communicating states model). Modes which accept less than 2% of the total energy are omitted in the table.

Table 16

Quotients of non-Condon and Condon rates k_{nC}/k_C and the nascent energy redistribution in S_0 in C_6D_6 (ν_4 non-Condon terms, communicating states model). Modes which accept less than 2% of the total energy are omitted in the table.

$$|< m|0 >_{nC} \;/\; < m|0 >_C|$$

m	ν_1	ν_2	ν_4
0	40	12	1.0×10^2
1	42	15	-
2	44	18	1.1×10^2
3	46	20	-
4	48	13	1.3×10^2
5	50	54	-
10	66	2.9×10^2	1.3×10^2
20	1.3×10^2	2.5×10^4	1.6×10^2
30	3.9×10^2	3.9×10^5	2.4×10^2
40	-	-	4.0×10^2
50	-	-	9.8×10^2
60	-	-	6.9×10^3

Table (1)

r	non-Condon case $Z(r)$	$\langle H(r) \rangle - \Delta E$	$\langle H^2(r) \rangle$	$z_2(r)$	$\langle h_2 \rangle$	$\langle h_2^2(r) \rangle$	Condon case $Z(r)$	$H(r) - \Delta E$	$\langle H^2(r) \rangle$	$z_2(r)$	$\langle h_2(r) \rangle$	$\langle h_2^2(r) \rangle$
1.43	7.02×10^4	10.8	16.4	2.50×10^5	8.89	0.28	5.23	2.88	17.6	18.3	0.84	0.57
1.41	1.01×10^5	8.91	5.84	4.25×10^4	8.81	0.42	3.73	0.87	5.95	15.7	0.75	0.40
1.39*	1.87×10^3	8.00	3.69	7.37×10^3	8.70	0.78	3.44	4.3×10^{-5}	3.25	13.6	0.68	0.29
1.37	4.06×10^2	7.29	3.69	1.32×10^3	8.46	1.81	3.64	-0.52	2.14	11.9	0.63	0.23
1.33	33.7	4.61	11.6	50.7	6.33	10.6	5.17	-1.16	1.19	9.44	0.55	0.16
1.31	17.3	2.01	12.8	21.7	3.92	1.20	6.67	-1.37	0.96	8.47	0.53	0.14
1.29**	14.4	4.83×10^{-6}	7.04	12.1	2.05	6.36	8.93	-1.55	0.80	7.65	0.50	0.12
1.27	16.1	-0.95	3.03	8.88	1.23	2.46	12.4	-1.70	0.68	6.94	0.48	0.11
1.25	20.4	-1.38	1.52	7.22	0.90	1.03	17.6	-1.82	0.59	6.32	0.46	0.10
1.23	27.6	-1.62	0.97	6.12	0.75	0.55	25.6	-1.93	0.52	5.78	0.44	0.09
1.11	3.05×10^3	-2.28	0.35	3.08	0.46	0.13	3.54×10^2	-2.40	0.30	3.64	0.34	0.07

Table (2)

	Single-mode			Complete basis set		
n_f	$S_1(n_f)$	$S_2(n_f)$	$S_3(n_f)$	$S_1(n_f)$	$S_2(n_f)$	$S_3(n_f)$
0	2.22	0.00	0.00	3.57	0.00	0.00
1	10.74	0.87	0.04	16.43	2.23	0.13
2	16.85	2.72	0.24	24.56	6.66	0.75
3	7.60	1.84	0.25	10.54	4.29	0.72
4	0.06	0.02	0.00	0.07	0.04	0.01
5	6.64	2.68	0.60	8.35	5.67	1.59
6	5.48	2.65	0.71	6.56	5.34	1.80
7	0.00	0.00	0.00	0.00	0.00	0.00
8	3.88	2.50	0.89	4.21	4.57	2.05
9	2.62	1.90	0.76	2.71	3.31	1.67
10	0.15	0.12	0.05	0.15	0.20	0.11
11	2.88	2.56	1.25	2.70	4.03	2.49
12	0.87	0.85	0.45	0.78	1.27	0.86
13	0.68	0.71	0.41	0.58	1.02	0.74
14	2.10	2.37	1.48	1.70	3.23	2.53
15	0.08	0.10	0.06	0.06	0.12	0.10
16	1.37	1.77	1.26	1.01	2.19	1.96
17	1.23	1.68	1.27	0.86	1.98	1.88
18	0.14	0.20	0.16	0.09	0.22	0.22
19	1.93	2.96	2.50	1.22	3.16	3.37
20	0.38	0.61	0.54	0.23	0.62	0.69
21	1.08	1.83	1.71	0.62	1.76	2.08
22	2.06	3.66	3.58	1.13	3.36	4.15
23	0.01	0.02	0.02	0.01	0.02	0.03
24	3.03	5.86	6.26	1.50	4.88	6.58
25	1.43	2.88	3.20	0.67	2.28	3.20
26	1.47	3.08	3.56	0.66	2.32	3.39
27	6.11	13.32	15.99	2.61	9.58	14.51
28	0.09	0.21	0.27	0.04	0.15	0.23
29	8.72	20.40	26.31	3.38	13.30	21.65
30	8.11	19.63	26.19	2.99	12.19	20.51

Table (3)

k_{nC}/k_C

ΔE	ν_2	ν_4
40	518	99
36	455	116
32	375	203
28	277	263
24	173	748
20	100	846
16	53	925
12	23	301

Table (4)

Accepted energy [%] in the

ΔE	k_{nC}/k_C	non-Condon case ν_1	ν_2	ν_4	ν_{13}	ν_{14}	ν_{20}	Condon case ν_1	ν_2	ν_4	ν_{13}	ν_{14}	ν_{20}
48	1.85	13.6	53.5	3.2	7.0	5.7	9.8	14.9	15.8	4.5	24.6	6.5	24.8
44	1.71	14.5	53.7	3.2	6.2	6.0	9.0	16.1	16.6	4.7	22.1	7.0	24.0
40	1.52	15.5	53.9	3.2	5.3	6.3	8.0	17.5	17.2	4.9	19.6	7.5	22.8
36	1.32	16.6	54.0	3.2	4.5	6.7	7.0	19.1	18.4	5.1	17.1	8.2	21.2
32	1.37	18.0	53.5	3.2	3.8	7.2	6.0	21.0	19.4	5.3	14.5	8.9	19.2
28	0.92	19.6	52.2	3.3	3.3	7.9	5.2	23.3	20.6	5.4	11.9	9.7	16.8
24	0.79	21.8	49.6	3.4	2.9	8.8	4.6	26.0	21.8	5.5	9.3	10.7	13.8
18	0.67	26.0	45.1	3.5	2.0	10.6	3.2	30.9	23.7	5.3	5.5	12.4	8.6
14	0.94	29.6	41.2	3.5	1.3	12.6	2.2	34.8	24.5	4.9	3.2	14.1	5.2
10	0.94	31.7	40.3	3.0	0.4	15.5	0.8	39.3	23.2	4.1	1.4	17.0	2.4

Table (5)

Accepted energy [%] in the

ΔE	k_{nC}/k_C	non-Condon case ν_1	ν_2	ν_8	ν_{14}	Condon case ν_1	ν_2	ν_4	ν_8	ν_{14}
48	0.75	19.4	9.7	9.4	42.9	19.4	8.0	6.1	9.6	44.2
44	0.78	20.8	10.6	9.4	40.1	20.9	8.5	6.2	9.6	41.5
40	0.80	22.4	11.5	9.4	37.1	22.5	9.2	6.2	9.6	38.7
36	0.84	24.2	12.7	9.2	34.1	24.4	10.0	6.2	9.4	35.8
32	0.87	26.3	14.0	8.8	31.1	26.6	10.8	6.2	4.6	32.9
28	0.91	28.7	15.4	8.2	28.0	29.1	11.7	6.0	8.6	30.0
24	0.97	31.2	17.1	7.2	25.2	31.9	12.8	5.7	8.0	27.2
20	1.03	34.0	19.1	6.2	22.6	35.1	13.8	5.4	7.0	24.6
16	1.10	36.9	21.5	4.8	20.4	38.8	14.7	5.0	5.6	22.6
12	1.15	39.2	24.3	3.2	19.3	42.7	15.0	4.5	4.2	21.6

Table (6)

k_{nC}/k_C

	C_6H_6			C_6D_6		
ΔE	ν_1	ν_4	ν_{14}	ν_1	ν_4	ν_{14}
48	0.88	-	-	1.08	0.61	10.1
44	0.93	-	-	1.17	0.61	7.3
40	0.99	1.47	0.56	1.27	0.61	5.3
38	1.03	1.47	0.56	1.33	0.61	4.6
36	1.07	1.47	0.57	1.40	0.61	4.0
34	1.13	1.47	0.57	1.48	0.61	3.5
30	1.26	1.47	0.58	1.69	0.60	-
26	1.44	2.73	0.58	1.98	0.57	-
22	1.70	1.88	-	2.36	0.56	-
18	2.05	-	-	2.78	0.53	-
14	5.59	-	-	3.21	0.53	-
10	3.50	-	-	6.77	0.56	-

Table (7)

$n_s(\nu_4)$	ΔE_{es}	k_{nC}/k_C	Accepted energy [%] in the non-Condon case						Condon case					
			ν_1	ν_2	ν_4	ν_{13}	ν_{14}	ν_{20}	ν_1	ν_2	ν_4	ν_{13}	ν_{14}	ν_{20}
0	0	0.6	18.2	17.5	10.1	16.1	7.8	20.1	18.3	18.0	5.0	18.2	7.9	22.0
1	365	0.83	17.5	15.8	25.7	10.2	7.3	14.0	17.8	16.8	15.8	11.0	7.6	18.0
2	730	1.11	16.7	14.2	37.8	6.5	6.9	9.5	17.2	15.6	25.9	10.5	7.2	14.2
3	1095	1.39	16.0	13.1	44.6	4.8	6.5	7.2	16.6	14.5	34.3	7.8	6.9	11.2
4	1460	1.68	15.3	12.1	50.6	3.4	6.2	5.3	16.0	13.5	41.2	6.0	6.6	8.8
5	1825	1.93	14.8	11.4	54.4	2.7	5.9	4.3	15.3	12.5	47.0	4.6	6.2	6.9
6	2190	2.18	14.2	10.6	58.2	2.1	5.7	3.3	14.7	11.7	51.8	3.6	5.9	5.5
8	2920	2.58	13.2	9.4	63.4	1.4	5.3	2.2	13.4	10.2	59.4	2.2	5.4	3.5
10	3650	2.89	12.3	8.4	67.4	0.9	5.0	1.5	12.3	8.9	65.1	1.4	5.0	2.3
15	5475	3.16	10.6	6.4	71.0	0.4	4.6	0.7	9.9	6.3	75.1	0.5	4.1	0.8
20	7300	2.90	9.2	4.8	78.7	0.2	4.2	0.3	7.9	4.2	81.6	0.2	3.6	0.3

Table (8)

Accepted energy [%] in the

$n_i(\nu_1)$	$\Delta E_{e,i}$	k_{nC}/k_C	non-Condon case ν_1	ν_2	ν_4	ν_8	ν_{14}	Condon case ν_1	ν_2	ν_4	ν_{14}
0	0	1.33	27.7	9.5	5.9	9.0	34.4	23.5	9.6	6.2	37.2
1	879	1.60	32.2	9.3	5.6	8.5	31.4	29.3	9.3	5.8	33.6
2	1758	1.90	35.9	9.2	5.3	8.0	29.1	34.0	9.0	5.5	30.8
3	2637	2.21	39.1	9.1	5.1	7.6	27.1	38.2	8.7	5.1	28.3
4	3515	2.54	42.1	8.9	4.9	7.2	25.3	42.0	8.4	4.8	26.2
5	4395	2.90	44.7	8.8	4.7	6.8	23.8	45.4	8.1	4.6	24.3
6	5274	3.31	47.0	8.7	4.5	6.5	22.5	48.5	7.9	4.3	22.6
7	6153	3.69	48.9	8.6	4.3	6.2	21.4	51.3	7.6	4.1	21.1
8	7032	4.00	50.3	8.5	4.2	6.0	20.6	54.0	7.4	3.9	19.7

Table (9)

$n_1(\nu_2)$	ΔE_{ex}	k_{nC}/k_C	Accepted energy [%] in the non-Condon case					Condon case				
			ν_1	ν_2	ν_4	ν_8	ν_{14}	ν_1	ν_2	ν_4	ν_8	ν_{14}
0	0	0.81	23.4	12.1	6.1	9.3	35.5	23.5	9.6	6.2	9.5	37.2
1	2340	1.02	23.1	16.4	5.8	8.8	32.8	22.0	17.1	5.7	8.7	33.5
2	4680	1.30	22.8	20.7	5.5	8.2	30.1	20.7	23.3	5.3	8.1	30.7
3	7020	1.70	22.4	25.3	5.1	7.6	27.4	19.5	28.7	4.9	7.5	28.2
4	9360	2.30	22.0	30.3	4.8	7.0	24.7	18.5	33.6	4.6	6.9	25.9

Table (10)

			Accepted energy [%] in the								
			non-Condon case					Condon case			
$n_i(\nu_4)$	ΔE_{ex}	k_{nC}/k_C	ν_1	ν_2	ν_4	ν_8	ν_{14}	ν_1	ν_2	ν_4	ν_{14}
0	0	0.60	23.0	9.3	14.5	8.5	31.7	23.5	9.6	6.2	37.2
1	306	0.84	21.7	8.8	28.8	6.6	23.1	22.6	9.2	17.8	29.7
2	612	1.10	20.5	8.2	38.7	5.2	17.9	21.6	8.7	27.5	21.0
3	918	1.36	19.6	7.8	44.5	4.4	15.3	20.6	8.3	35.2	20.0
4	1224	1.61	18.6	7.3	49.8	3.7	13.1	19.7	7.9	41.4	17.0
5	1530	1.84	17.9	7.0	53.3	3.2	11.8	18.8	7.5	46.5	14.8
6	1836	2.10	17.1	6.6	56.8	2.8	10.5	18.0	7.1	50.8	13.0
8	2448	2.50	15.9	6.0	61.9	2.2	8.9	16.2	6.4	57.8	10.5
12	3672	3.10	13.8	4.9	69.0	1.4	7.0	13.8	5.1	67.6	7.5
16	4896	3.31	12.1	4.0	73.9	1.0	5.9	11.6	4.0	74.3	5.8
20	6120	3.26	10.8	3.3	77.4	0.7	5.3	9.8	3.1	79.3	4.8

Table (11)

			Accepted energy [%] in the									
			non-Condon case					Condon case				
$n_i(\nu_{14})$	ΔE_{ex}	k_{nC}/k_C	ν_1	ν_2	ν_4	ν_8	ν_{14}	ν_1	ν_2	ν_4	ν_8	ν_{14}
0	0	1.39	23.3	9.5	6.0	9.2	38.2	25.2	10.4	8.8	14.0	24.1
1	1566.8	1.67	21.9	8.9	4.7	6.9	46.4	22.8	9.3	6.2	9.6	38.3
2	3133.6	2.00	20.6	8.3	3.8	5.4	52.3	20.9	8.5	4.9	7.3	47.0
3	4700.4	1.97	20.0	8.0	3.5	4.8	54.6	19.3	7.8	4.1	5.9	53.1
4	6267.2	3.00	19.2	7.6	3.1	4.1	57.9	18.0	7.2	3.5	4.9	57.8
5	7834.0	1.90	19.2	7.6	3.1	4.1	58.0	16.8	6.7	3.0	4.2	61.6
6	9100.8	2.17	18.6	7.3	2.9	3.7	60.2	15.8	6.3	2.7	3.6	64.8

Table (12)

ΔE_{ex}	k_{nC}/k_C	Accepted energy [%]							
		ν_1	ν_2	ν_4	ν_{10}	ν_{13}	ν_{14}	ν_{16}	ν_{20}
0.5	2.84	15.6	52.4	3.5	2.5	4.6	6.0	0.9	6.9
396.2	1.66	15.5	38.2	17.5	2.8	4.1	5.9	2.0	6.2
835.4	0.96	13.5	13.6	52.0	2.7	1.5	5.0	2.8	2.4
1776.2	0.75	10.9	8.2	64.0	2.6	0.3	4.1	3.8	0.5
2770.7	0.67	9.7	6.1	67.4	2.6	0.1	3.7	4.8	0.1
3914.2	0.63	8.9	4.7	68.7	2.8	0.0	3.5	5.7	0.0
5176.8	0.60	8.4	3.8	68.8	3.0	0.0	3.1	6.6	0.1
6536.6	0.60	8.0	3.2	68.4	3.2	0.1	3.2	7.4	0.1

Table (13)

Accepted energy [%]

ΔE_{ex}	k_{nC}/k_C	ν_1	ν_2	ν_4	ν_8	ν_{10}	ν_{14}	ν_{16}	ν_{17}
0	1.34	27.0	9.1	6.1	9.2	2.0	33.0	0.8	2.2
289.4	1.14	22.7	7.6	37.0	4.9	2.0	15.3	1.6	1.9
853.2	0.85	16.0	4.9	61.2	1.9	1.9	6.7	2.5	1.5
1235.6	0.77	13.9	3.9	66.1	1.4	1.9	5.4	2.9	1.5
1671.6	0.74	12.5	3.2	69.1	1.1	1.9	4.7	3.3	1.4
2136.1	0.71	11.4	2.6	70.8	0.9	2.0	4.3	3.7	1.4
2696.2	0.69	10.6	2.2	71.7	0.7	2.1	4.0	4.2	1.5
3268.4	0.67	10.0	1.9	72.2	0.4	2.2	3.8	4.6	1.5
3875.9	0.66	9.6	1.7	72.4	0.2	2.3	3.7	5.0	1.6
6595.5	0.63	8.5	1.2	71.5	0.0	2.8	3.3	6.7	1.8

Table (14)

Accepted energy [%]

ΔE_{ex}	k_{nC}/k_C	ν_1	ν_2	ν_4	ν_8	ν_{10}	ν_{14}	ν_{16}	ν_{17}
0	0.82	22.8	11.7	6.3	9.4	2.0	34.1	0.8	2.2
290.9	0.75	19.5	9.2	38.5	5.0	2.0	15.4	1.6	1.9
540.8	0.69	16.4	7.4	53.9	2.9	1.9	9.2	2.0	1.7
866.3	0.65	14.0	5.9	62.1	1.9	1.9	6.7	2.5	1.5
1713.0	0.60	11.1	4.0	69.6	1.1	1.9	4.7	3.3	1.4
2769.6	0.57	9.5	2.9	72.2	0.7	2.1	4.0	4.2	1.5
3361.2	0.55	9.0	2.5	72.7	0.5	2.2	3.8	4.6	1.5
4648.5	0.54	8.2	2.0	72.9	0.3	2.4	3.5	5.4	1.6
6787.9	0.53	7.6	1.5	72.0	0.1	2.8	3.3	6.7	1.8

Table (15)

Accepted energy [%]

ΔE_{ex}	k_{nC}/k_C	ν_1	ν_2	ν_4	ν_8	ν_{10}	ν_{14}	ν_{16}	ν_{17}
0.0	0.72	22.4	9.0	14.4	8.7	2.0	30.4	0.8	2.2
180.1	0.96	20.7	8.3	31.6	6.3	1.9	20.0	1.2	2.0
436.8	2.20	18.4	7.2	46.1	4.2	1.9	12.9	1.6	1.8
822.6	2.84	16.2	6.1	55.7	2.8	1.9	9.0	2.0	1.7
1331.9	2.60	14.5	5.1	61.4	2.0	1.9	7.1	2.5	1.6
2673.5	1.26	12.6	3.9	65.7	1.4	2.2	5.4	3.9	1.6
3481.3	0.79	12.1	3.5	65.9	1.2	2.4	5.1	4.9	1.7
5320.6	0.32	11.5	3.0	64.0	0.7	2.9	4.6	7.6	1.9
6336.2	0.22	11.3	2.8	62.2	0.5	3.2	4.4	9.6	2.0

Table (16)