

FRANCK-CONDON EFFECTS IN RESONANCE RAMAN SPECTRA OF TCNQ^- AND $\text{C}_{10}\text{H}_8^+$ RADICALS. A SEARCH FOR DUSHINSKY ROTATION OF TOTALLY SYMMETRIC MODES

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The resonance Raman spectra of tetracyanoquinodimethane anion (TCNQ^-) and naphthalene cation ($\text{C}_{10}\text{H}_8^+$) are analyzed in terms of theoretical model based on the Franck-Condon effects. The model includes also the effect of rotation of totally symmetric normal coordinates upon electronic excitation to the resonant state (Dushinsky effects). It is shown that such a simple model accounts correctly for the available resonance Raman spectra for TCNQ^- and $\text{C}_{10}\text{H}_8^+$ radicals. The possible model refinements such as vibronic coupling effects are also briefly discussed.

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1. Introduction

An excitation of a molecule to its single electronic state tends to enhance the totally symmetric progressions in the resonance Raman (RR) spectra. The intensity distribution in these progressions is governed by vibrational overlap integrals resulting from Franck-Condon (FC) principle [1, 2] known from the theory of electronic emission and absorption spectra. In contrast to the emission and absorption phenomena, in the resonance Raman scattering the individual FC factors entering the scattering tensor are modulated by the complex energy denominators so that the interferences will occur between different scattering channels. Although these effects complicate an analysis of experimental data, the literature of last years has shown that the theoretical approaches based on the FC principle have no difficulties to explain the main features of the measured excitation profiles (EPs) of totally symmetric modes [2-8].

The complications may arise from the fact that the vibrational coordinates should not be literally treated to be the same in the ground and in excited electronic state(s). By a traditional choice, the vibrations in the ground state are conveniently represented by the normal coordinates, in terms of which the vibrational potential has a simple diagonal quadratic form. In the normal modes representation, the excited state potential(s) will generally contain bilinear Q -dependent terms. It means that the normal coordinates of the same symmetry can mix in the excited state(s). This effect is well-known and is referred to as the normal-mode mixing, the multimode rotation or Dushinsky effect [5].

The fact that the normal coordinates can lose their identity following electronic excitation can have important implications for the absorption, the emission and the resonance Raman scattering as well. One can show that the normal-mode mixing can cause the intensity transfer among the levels of vibrational manifolds belonging to different normal modes [5]. If such a mixing is not very weak, the disappearance of certain bands in emission and the enhancement of others in the absorption will occur [5, 9]. Such behavior upsets the mirror-image symmetry between absorption and emission spectra and, by implication, the RR progressions of totally symmetric modes cease to resemble those resulting entirely from FC effects.

In this paper we attempt to look for the Dushinsky effect in the excited states of some anion and cation radicals. Of the limited number of radicals studied by the RR technique we can indicate three radicals: tetracyanoquinodimethane anion (TCNQ⁻), naphthalene cation (C₁₀H₈⁺) and pyromellitic dianhydride anion (PMDA⁻). The electronic structure of these radicals are well-known [10–13] and their RR spectra are mostly due to activity of totally symmetric vibrations [13, 14]. For quantitative analysis we have chosen two radicals, namely, TCNQ⁻ and C₁₀H₈⁺. The resonance Raman excitation profiles for two selectively chosen vibrations of TCNQ⁻ were already discussed in some detail earlier [4]. Since the quantitative interpretation of RR spectra of C₁₀H₈⁺ was not carried out so far we will do it in the present study. To achieve this goal we apply the simple model based on the same assumptions as that already reported [4, 5]. This model leads to reasonable reconstructions of RR spectra for both radicals studied. We shall show, however, that some drawbacks can arise when studying RR spectra of C₁₀H₈⁺ radical. It claims for the model refinements that are also discussed.

2. Model

We consider the ground state Φ_0 and an excited electronic state Φ_m and use the adiabatic Born–Oppenheimer approximation. In that approximation the vibronic functions $\Psi_{0\mathbf{k}}$ and $\Psi_{m\mathbf{v}}$ that act as the initial, final and the intermediate states in the resonance Raman scattering can be written as

$$\Psi_{0\mathbf{k}} = \Phi_0(q; Q)\xi_{0\mathbf{k}}(Q),$$

$$\Psi_{m\mathbf{v}} = \Phi_m(q; Q)\xi_{m\mathbf{v}}(Q), \quad (1)$$

where $\xi_{0\mathbf{k}}(Q)$ and $\xi_{m\mathbf{v}}(Q)$ are the vibrational wave functions representing, respectively the ground and excited state vibrational manifolds; \mathbf{k} and \mathbf{v} being the sets of

vibrational quantum numbers. We assume that the vibrational manifolds of Φ_0 and Φ_m states are adequately described by N harmonic totally symmetric oscillators represented by the set of mass-weighted normal coordinates Q . These oscillators are displaced and the corresponding coordinates are rotated in the excited states relative to the ground state. Therefore, if the ground-state potential is given by

$$E_0(Q) = E_0(0) + \frac{1}{2} \sum_{i=1}^N \omega_{0i}^2 Q_i^2 \quad (2)$$

that in the excited state Φ_m will take the form

$$E_m(Q) = E_m(0) + \sum_{i=1}^N \omega_{mi}^{3/2} B_{mi} Q_i + \frac{1}{2} \sum_{i=1}^N \omega_{mi}^2 Q_i^2 + \sum \sum_{i>j} (\omega_{mi} \omega_{mj})^{1/2} f_{ij} Q_i Q_j, \quad (3)$$

where $E_0(0)$ and $E_m(0)$ are the electronic energies given in the fixed ground state nuclear equilibrium configuration. B_{mi} is a dimensionless displacement (FC) parameter of the i -th mode in the m -th electronic state. The quadratic form coefficients, f_{ij} , are Dushinsky parameters due to rotation of the m -th state potential surface relative to that in the ground state.

Now let us consider the resonance Raman transition realized through the absorption-emission channel $\Psi_{00} \rightarrow \Psi_{mv} \rightarrow \Psi_{0k}$ characterized by the Cartesian scattering tensor [2]

$$\alpha_{\sigma\rho}(0 \rightarrow k) = \sum_{V_1} \cdots \sum_{V_i} \cdots \sum_{V_N} \frac{(\langle \Psi_{0k} | \hat{D}_\sigma | \Psi_{mv} \rangle)(\langle \Psi_{mv} | \hat{D}_\rho | \Psi_{00} \rangle)}{E_{mv} - E_{00} - \Omega - i\Gamma_{mv}}, \quad (4)$$

where $\langle \cdots \rangle$ and (\cdots) denote the integration over the electronic and vibrational coordinates, respectively. E_{mv} is the energy of the intermediate state with the linewidth Γ_{mv} describing homogeneous broadening through radiative and (predominantly) non-radiative damping. Ω is the energy of laser light in units $\hbar = 1$. Within Condon approximation [15], the transition dipole matrix elements $\langle \Phi_0 | \hat{D} | \Phi_m \rangle$ and $\langle \Phi_m | \hat{D} | \Phi_0 \rangle$ can be considered to be only weakly Q -dependent. At this level, the integrals in the numerator of Eq. (4) can be evaluated from

$$\begin{aligned} (\langle \Psi_{0k} | \hat{D} | \Psi_{mv} \rangle) &= \langle \Psi_0 | \hat{D} | \Psi_m \rangle (\xi_{0k} | \xi_{mv}) \equiv D_{0m}^0 (\xi_{0k} | \xi_{mv}), \\ (\langle \Psi_{mv} | \hat{D} | \Psi_{00} \rangle) &= \langle \Psi_m | \hat{D} | \Psi_0 \rangle (\xi_{mv} | \xi_{00}) \equiv D_{0m}^0 (\xi_{mv} | \xi_{00}), \end{aligned} \quad (5)$$

where $(\xi_{mv} | \xi_{00})$ and $(\xi_{0k} | \xi_{mv})$ are the vibrational overlap integrals. Without losing generality we will assume that the electronic transition dipole moment D_{0m}^0 is polarized along the x -axis of a molecule. Therefore, inserting (5) into (4) we get

$$\alpha_{xx}(0 \rightarrow k) = |D_{0m}^0|^2 \sum_{V_1} \cdots \sum_{V_i} \cdots \sum_{V_N} \frac{(\xi_{0k} | \xi_{mv})(\xi_{mv} | \xi_{00})}{E_{mv} - E_{00} - \Omega - i\Gamma_{mv}}. \quad (6)$$

The vibrational overlap integrals $(\xi_{mv} | \xi_{00})$ and $(\xi_{0k} | \xi_{mv})$ have simple analytical forms [3] only if the third term in Eq. (3) is negligible. Otherwise, the numerical treatment is generally required to determine both the energies, E_{mv} , and the

vibrational overlap integrals in Eq. (6). It can be done by a standard numerical procedure.

The Raman spectra presented in subsequent section were calculated as the square of the tensor element (6) multiplied by fourth power of the energy of the scattered light. In these calculations linewidths Γ_{mv} were assumed to be the same for all vibrational levels. No attempt was made to include inhomogeneous broadening [16] due to different local environments for different molecules in the sample, and coupling with "solvent" vibrations [17] leading to an excitation of low-frequency solvent modes during the scattering. To reduce the number of parameters we also assumed that the vibrational frequencies are the same in all electronic states considered.

3. Application

To our best knowledge the number of cation and anion radicals studied by RR technique is not large. Here we can mention TCNQ⁻, C₁₀H₈⁺ and pyromellitic dianhydride anion [13, 14]. Even smaller is the number of radicals for which excitation profiles were measured over the extensive laser excitation range. For the purpose of this paper we have chosen two radicals: TCNQ⁻ and C₁₀H₈⁺ for which the available RR experimental data seem to be sufficiently complete to allow their quantitative interpretation on the base of the model presented in the previous section. Because of multimode character of that model some ambiguities may arise when trying to determine the model parameters from the absorption spectra of molecule considered. To avoid that problem and to show how the Dushinsky rotation can affect RR spectra we applied the following procedure justifiable when f_{ij} in Eq. (3) are small. First, the FC parameters, B_{mi} , are extracted from well-resolved experimental absorption spectra under assumption that Dushinsky rotations can be entirely neglected. The FC parameters obtained in that way are subsequently used to calculate RR spectra. Then, the same is done in the presence of small (assumed) Dushinsky rotation of selectively chosen pair(s) of normal coordinates. According to this procedure the RR theoretical spectra reported in subsequent sections for TCNQ⁻, C₁₀H₈⁺ are determined by the set of parameters available from the experimental absorption spectra.

3.1. TCNQ anion

In the range of 11500–28000 cm⁻¹ the absorption spectrum of TCNQ⁻ reveals two prominent bands [13]. Of these two bands, the low-energy one results from an allowed ${}^2B_{3g} \rightarrow {}^2B_{1u}$ electronic transition with the origin located at 11872 cm⁻¹. Of ten possible totally symmetric vibrations of TCNQ⁻, only five vibrations with ground state frequencies: $\omega_1 = 336$ cm⁻¹, $\omega_2 = 1195$ cm⁻¹, $\omega_3 = 1389$ cm⁻¹, $\omega_4 = 1613$ cm⁻¹ and $\omega_5 = 2192$ cm⁻¹ constitute the well-resolved structure of the ${}^2B_{3g} \rightarrow {}^2B_{1u}$ transition. With an exception for ω_5 -mode, the four totally symmetric vibrations are strongly enhanced as fundamentals in the RR spectrum when exciting TCNQ⁻ by the krypton laser line at 15454 cm⁻¹ (6471 Å). Since these fundamental transitions show no dispersion of depolarization ratios ($\rho = 1/3$), the assignment of active modes is unquestionable. It also

indicates that only single diagonal element of the Raman tensor contributes substantially to the scattering.

Figure 1 shows the experimental absorption spectrum and its theoretical reconstruction obtained in the absence of Dushinsky rotation (Fig. 1b) and with a small rotation within two pairs (Q_1, Q_2) and (Q_3, Q_4) of normal coordinates (Fig. 1c). The corresponding RR spectra calculated for the laser excitation energy: $\Omega = 15454 \text{ cm}^{-1}$ are also given in Fig. 1a-c. In computations, the linewidth $\Gamma = 170 \text{ cm}^{-1}$ due to radiative and non-radiative effects was applied.

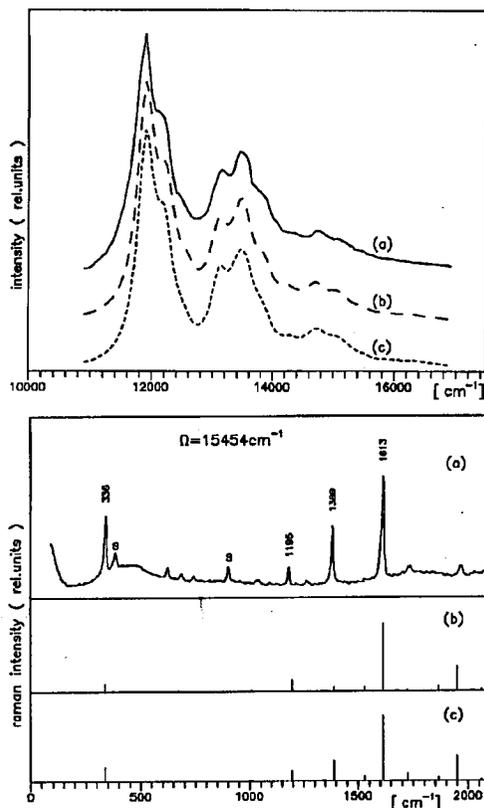


Fig. 1. The absorption (top) and RR spectra of TCNQ^- (bottom) for $\Omega = 15454 \text{ cm}^{-1}$: (a) the experiment, (b) without mode-mixing and (c) with mode-mixing of (Q_1, Q_2) and (Q_3, Q_4) pairs of coordinates. The model parameters are given in Table.

As can be seen from Fig. 1, the theoretical model reproduces very well the experimental absorption spectrum. The small rotation of two selectively chosen vibrations does not affect much the absorption band-shape. It suggests that the normal-mode mixing in the ${}^2B_{1u}$ state of TCNQ^- should not be large. We checked that small changes in Dushinsky parameters within other pairs of vibrations only slightly influences the absorption spectrum. However, the mixing within pairs

(Q_1, Q_2) and (Q_3, Q_4) of normal coordinates reproduces the Raman intensities of ω_2 and ω_3 fundamentals much better than the FC effect alone does. It may be an indication of the normal-mode mixing within pairs (Q_1, Q_2) and (Q_3, Q_4) of normal coordinates. In the interest of clarity we wish to stress that the results shown in Fig. 1 do not provide a unique evidence of Dushinsky rotation. It would be presumptuous to claim a single RR spectrum to support for the normal-mode mixing without considering other (hopefully marginal) model refinements such as, for example, an anharmonicity of active vibrations. Without these refinements nothing more can be said in the matter concerning this subsection.

3.2. $C_{10}H_8$ cation

The absorption spectrum of $C_{10}H_8^+$ observed in the range of 14000–19000 cm^{-1} corresponds to ${}^2A_u \rightarrow {}^2B_{1g}$ electronic transition [12]. The vibrational structure of this transition is dominated by the three totally symmetric vibrations with the ground state frequencies: $\omega_1 = 511 \text{ cm}^{-1}$, $\omega_2 = 769 \text{ cm}^{-1}$ and $\omega_3 = 1398 \text{ cm}^{-1}$; the ω_2 mode being the weakest of the three seen in the absorption. Since the number of active vibrations is small, the values of FC parameters could be estimated by the trial and error directly from the well resolved absorption spectrum. The analysis yields: $B_1 = 1.00$, $B_2 = 0.49$, $B_3 = 1.06$ and $B_1 = 1.26$, $B_2 = 0.49$, $B_3 = 1.06$. This latter set amounts to the assumption that Q_1 and Q_3 vibrations are involved in Dushinsky rotation. These parameters together with others used in calculations are collected in Table. For both sets of parameters, the calculated absorption and RR spectra at the origin of the absorption band ($\Omega = 14535 \text{ cm}^{-1}$) are given in Fig. 2b and Fig. 2c.

TABLE
Parameters values applied to recalculate the observed absorption and to calculate RR spectra.

TCNQ ⁻							
B_1	B_2	B_3	B_4	$f_{12}^{a,b}$	f_{13}	f_{34}	$\Gamma^{b,c}$
1.00	0.79	0.37	0.75	0.0	0.0	0.0	170.0
1.59	0.88	0.59	0.62	250.0	0.0	175.0	170.0
$C_{10}H_8^+$							
1.00	0.49	1.06	–	0.0	0.0	–	135.0
1.26	0.49	1.06	–	0.0	125.0	–	135.0

^aremaining Dushinsky parameters are equated to zero,

^bin cm^{-1} ,

^c $\Gamma_{mi} = \Gamma$ for all i .

A look at Fig. 2 reveals that the model accounts correctly for the observed intensity distribution in the RR spectrum. It is also seen that the normal-mode mixing of Q_1 and Q_3 coordinates only slightly influences the RR spectrum. Such

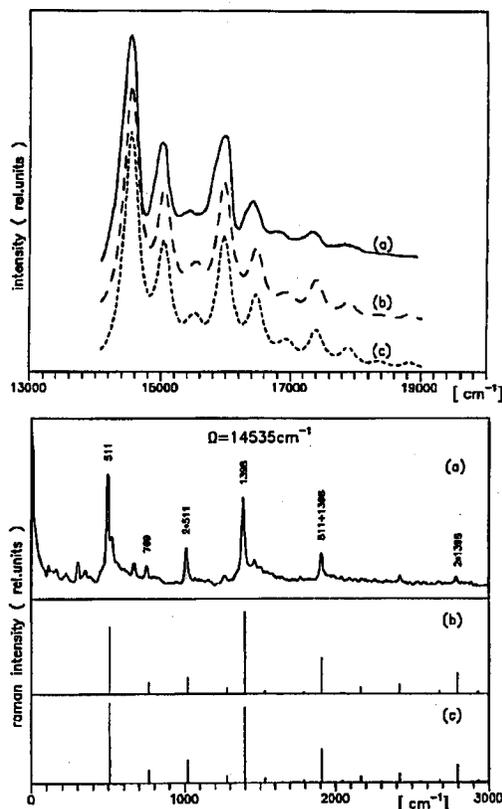


Fig. 2. The absorption (top) and RR spectra of $C_{10}H_8^+$ (bottom) for $\Omega = 14535 \text{ cm}^{-1}$: (a) the experiment, (b) without mode-mixing and (c) with mode-mixing of Q_1 and Q_3 coordinates. The model parameters are given in Table.

a result was expected since a weak normal-mode mixing should not strongly affect the RR spectra observed under the resonance with the absorption origin [5].

In Fig. 3, we compare the experimental and the theoretical RR spectra obtained for the excitation energies: $\Omega = 15060 \text{ cm}^{-1}$ and $\Omega = 16000 \text{ cm}^{-1}$ that correspond approximately to energies of one quantum levels of ω_1 and ω_3 vibrations in the excited state. The model parameters used in the computations were the same as those for Fig. 2. Apart from the substantial amount of "noise" in the region 200–1000 cm^{-1} , due to Raman bands of Freon glass [14], the RR spectra are dominated by the overtones and combinations bands. This feature is quite well reproduced by the model applied with reasonable values of FC parameters. Once again the normal-mode mixing only slightly influences the RR spectra so that the reasonable agreement with the experiment could be also achieved in the absence of Dushinsky effect.

Viewing systematically the RR spectra shown in Figs. 2 and 3, we can see that the progressions involving the ω_3 vibration bring too much intensity as com-

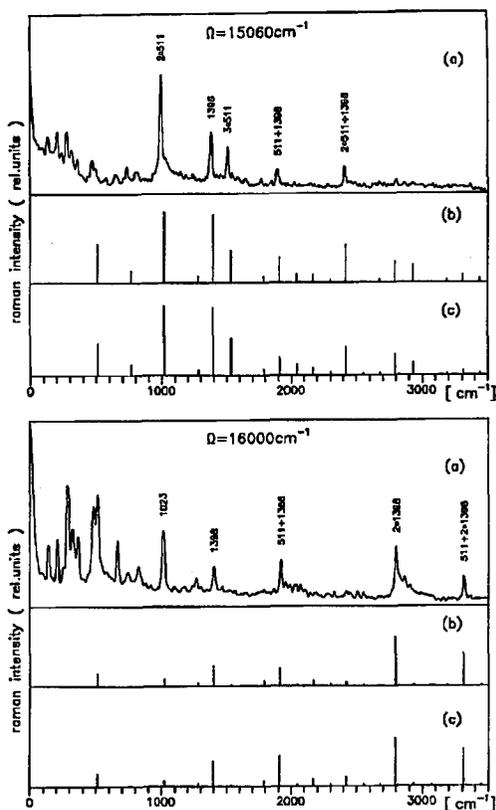


Fig. 3. The RR spectra of $C_{10}H_8^+$ calculated at $\Omega = 15060 \text{ cm}^{-1}$ (top) and $\Omega = 16000 \text{ cm}^{-1}$ (bottom). The model parameters and the plot arrangement are the same as for RR spectra in Fig. 2.

paring to their experimental counterparts. Alternatively we can say that the FC parameter $B_3 = 1.06$ used to reproduce the absorption spectrum was overestimated comparing to that needed in RR spectra calculations. This is immediately seen from an analysis based on the expression [6]

$$I(\omega_3) : I(2\omega_3) = B_3^2 : \frac{1}{2}B_3^4, \quad (7)$$

which is valid to very good approximation when the Raman intensities of the fundamental, $I(\omega_3)$, and first overtone, $I(2\omega_3)$, are taken from the RR spectrum measured at the origin of the well-resolved absorption band. With the ratio $I(2\omega_3)/I(\omega_3) \approx 0.15$ available from the Raman spectrum the relation (7) yields $B_3 \approx 0.55$. This value of B_3 would be too small to account satisfactorily for the intensity distribution in the absorption spectra. It indicates that some effects may be missed in the model applied in this paper.

In our opinion it is unlikely that an anharmonicity of the totally symmetric vibrations could be responsible for the discrepancy envisaged. The small change of

the frequency of the ω_3 vibration upon electronic excitation is also not expected to suppress sufficiently strong the intensities in Raman progressions of that mode. However it is very likely that vibronic coupling together with Franck-Condon effects ought to be examined in order to obtain a complete and more accurate picture of the vibrational structure of RR spectra. In fact the vibronic coupling can cause that the electronic transition dipole moment $\langle \Psi_0 | \mathbf{D} | \Psi_m \rangle$ will depend on the normal coordinates violating the Condon approximation used to simplify the relations (5). To illustrate the effect let us assume a single mode approximation and let the vibronic coupling be tractable in the lowest order of perturbational approach. At this stage the terms required to calculate the numerator in Eq. (4) can be written as

$$\begin{aligned} & (\langle \Psi_{0k} | \hat{D} | \Psi_{mv} \rangle) (\langle \Psi_{mv} | \hat{D} | \Psi_{00} \rangle) \approx |D_{0m}^0|^2 (\xi_{0k} | \xi_{mv}) (\xi_{mv} | \xi_{00}) \\ & + \sum_k D_{0k} D_{0m} \bar{\lambda}_{km} [(\xi_{0k} | Q | \xi_{mv}) (\xi_{mv} | \xi_{00}) + (\xi_{0k} | \xi_{mv}) (\xi_{mv} | Q | \xi_{00})], \quad (8) \end{aligned}$$

where the coefficients $\bar{\lambda}_{km} = \langle \Phi_k^0 | \hat{H}'_{el} | \Phi_m^0 \rangle (E_k(0) - E_m(0))^{-1}$ are due to vibronic coupling; \hat{H}'_{el} being a derivative of the electronic Hamiltonian with respect to normal coordinate Q . The sum in (8) runs over all electronic states involved in the vibronic coupling to m -th state. The corresponding matrix elements for the absorption read

$$\begin{aligned} & |(\langle \Psi_{00} | \hat{D} | \Psi_{mv} \rangle)|^2 \approx |D_{0m}^0|^2 |(\xi_{00} | \xi_{mv})|^2 \\ & + 2 \sum_k D_{0k} D_{0m} \lambda_{km} (\xi_{00} | Q | \xi_{mv}) (\xi_{mv} | \xi_{00}). \quad (9) \end{aligned}$$

From expressions (8) and (9) one can see that the only leading terms enter the model used in this paper. The remaining terms stand as the corrections due to vibronic couplings effects. These correction terms are not necessarily negligible since potentially a vast number of electronic states can be involved in the vibronic coupling. Moreover the correction terms in expressions (8) and (9) are governed by different types of vibrational integrals. It means that the vibronic coupling will affect the absorption and RR spectra in a different way. However, to deal with these problems and to earn more information from the experimental RR spectra of $C_{10}H_8^{\ddagger}$ radical, the introduction of additional model parameters would be required. For this reason, we will not carry this discussion further.

4. Conclusion

The results presented in this paper leave little doubts that the vibrational structures of RR spectra of $TCNQ^-$ and $C_{10}H_8^{\ddagger}$ radicals are mainly due to FC effects. The hopefully small corrections due vibronic coupling effects are likely, especially for the $C_{10}H_8^{\ddagger}$ radical for which the actual model overestimates the intensity in the progressions of the ω_3 vibration. On the other hand, the scarce experimental data available provides no prima facie evidence of Dushinsky effect in the low-energy states of $TCNQ^-$ and $C_{10}H_8^{\ddagger}$ radicals. However, the analysis made in this paper suggests that a small normal-mode mixing in the low-energy

states of these radicals is plausible and should not be ignored a priori in the future studies. Unfortunately, the magnitude of that mixing cannot be assessed without detailed force-field calculations for the ground and excited states. At present time we are pursuing such calculations.

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