Electronic spectroscopy in condensed media: Spectra of styrene and cyclo-octatetraene anions

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A general theoretical formalism developed in earlier publications for treating the electronic spectra of solvated anions is found to successfully describe the spectra of styrene and cyclooctatetraene anions in MTHF glass at 77°K. The analysis provided supports the conclusions that the first two excited states of the styrene anion and the first excited state of the cyclo-octatetraene anion in solution have sufficiently long lifetimes (> 10^{-11} sec) so as to have negligible lifetime broadening of their spectra. The entire widths of the observed spectra can be accounted for via Franck-Condon progressions alone; the degree of structure in the experimental spectra provide information about solvent inhomogeneous broadening.

I. INTRODUCTION

We have recently developed a general theoretical formalism for treating the electronic spectroscopy of molecular anions in one- and two-component solutions. In this series of articles, of which the present manuscript is the fourth member, our goals are to test the predictive capabilities of our theoretical model and, for systems where the needed isolated-molecule information is incomplete, to extract information about the anion-solvent interaction by comparing the theoretical and experimentally observed spectra.

The optical absorption spectrum of cyclo-octatetraene anion (COT^-) and both experimental and theoretical studies of the styrene anion (St^-) in methyl tetrahydrofuran glass (MTHF) at 77°K are the subjects of considerations in this paper. In the gas phase, all of the negative ion states of styrene autodetach with lifetimes between 10^{-14} and 10^{-10} sec. While the ground state of isolated COT^- is stable with respect to electron loss, the excited states of this anion autodetach with lifetimes ≤10^{-14} sec. It is generally known that, in condensed phases (for example, in solutions or in hydrocarbon glasses), the electronic states of anions become stabilized to an extent which often places the ground and low-lying excited states below the neutral molecule state. As is discussed in more detail later in this paper, it is likely that the ground state of St^- and the first excited state of COT^- undergo such stabilization in the MTHF glass.

Based upon evidence presented in this work, it is also likely that the lifetimes of the first and second excited states of St^- and the first excited state of COT^- increase in solution to an extent such that their contribution to broadening of the optical line shape is negligible (τ > 10^{-14} sec).

In the following section, we review the theoretical model introduced in Refs. 1-3. Section III contains an analysis of the results of our approach as applied to the experimental COT^- and St^- anion spectra. In Sec. IV, we make our concluding remarks.

II. SPECTRAL THEORY

In earlier publications, a general theory of the optical spectra of solvated anions, electrons, and charge-transfer complexes was described. To facilitate discussion of those approximations which are specific to the systems under consideration here, we now summarize the salient points of the earlier development.

In studying a dynamical property of a molecule (e.g., electronic-vibrational spectra in solution) which is not strongly perturbed by a external medium in thermal equilibrium, it is possible, as demonstrated earlier, to eliminate the detailed dynamics of the medium from explicit consideration. The effects of the medium are, in essence, replaced by a fluctuating external potential which acts upon the solute species under study.

Applying this line of reasoning to the problem at hand, the electronic absorption band shape I(ω) is related to the correlation function 〈F(t)F(0)〉 of the electronic dipole operator F(t) via a Fourier transform:

\[ I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle F(t)F(0) \rangle, \]  

with

\[ \langle F(t)F(0) \rangle = \text{Tr}_R \left[ \rho(R) \text{Tr}_V \left[ f(r) \exp(iHt) F(0) \exp(-iHt) F(0) \right] \right], \]  

where ρ(R) and f(r) are the distribution functions describing the initial values of the coordinates of the medium and the molecule, respectively.

Next, one makes the following partition of the total Hamiltonian:

\[ H(r,R) = H^0(r,R) + V(r,R), \]  

where

\[ H^0(r,R) = \left[ T(R) + U(R) \right] + \left[ h(r) + \bar{u}(r) \right] \]  

describes the motion of the medium in the absence of the molecule [via T(R) + U(R)] and the motion of the molecule in the equilibrium averaged field of the medium \( \bar{u} \) [via \( h(r) + \bar{u}(r) \)]. The fluctuation potential \( V(r,R) = \bar{u}(r,R) - \bar{u}(r) \) contains the effects of deviations of the medium away from its equilibrium coordinates. The average potential \( \bar{u} \) contains the static solvation effects of the medium, whereas \( V \) contributes to perturbations on the solute whenever the solvent fluctuates away from its equilibrium averaged coordinates.

Then, use of the operator identity
\[
\exp(i\mathcal{H}t) = \exp(i\mathcal{H}_0 t) \exp\left[ i \int_0^t \mathcal{V}(\tau) d\tau \right], \tag{5}
\]
where
\[
\mathcal{V}(\tau) = \exp(-i\mathcal{H}_0 \tau) \mathcal{V} \exp(i\mathcal{H}_0 \tau)
\]
allows us to rewrite the above correlation function in a form in which the dynamics of the medium have been averaged over and, in effect, eliminated from explicit consideration:
\[
\langle \mathcal{F}(t) \mathcal{F}(0) \rangle = \langle \exp\left[ i(h + \mathcal{V} t) \right] \mathcal{F} \exp(-i(h + \mathcal{V} t)) \rangle, \tag{7}
\]
with
\[
\mathcal{F} = \exp\left[ i \int_0^t \mathcal{V}(\tau) d\tau \right] \mathcal{F} \exp\left[-i \int_0^t \mathcal{V}(\tau) d\tau \right]. \tag{8}
\]
where the subscripts \( r \) and \( R \) denote averaging over the initial values of the molecule and medium coordinates, respectively. \( \mathcal{F} \) is now only a function of the molecule's coordinates \( r \).

The next step in the development of our working equations involves simplifications based upon the following physically motivated approximations: (i) The vibrational and rotational–translational degrees of freedom of the medium are assumed to be decoupled, thus allowing the averaging \( \langle \cdot \rangle_R \) to be performed separately over these respective coordinates and momenta. (ii) The electronic transition under study is assumed to occur in a short time relative to the time scale for variations in the solute's and solvent's vibrational, rotational, and translational coordinates. This assumption permits the intensities of each vibrational line in the electronic transition to be expressed explicitly in terms of the Franck–Condon (F–C) overlaps between the vibrational functions of the absorbing species (labeled O) and those of the species on which the excitation resides after the absorption takes place (labeled S). For charge transfer spectra, these species are the donor and the acceptor, respectively. For solution-phase anion spectra, the possibilities of both localized (on a single solute anion for which \( O=S \)) and charge transfer (of an electron to a neighboring solute molecule for which \( O=S \)) must, in general, be treated. The resulting F–C factors are denoted here by
\[
F_{\alpha\beta}(v_1, \tilde{v}_1) = \langle \psi_{\lambda_0} \mid \tilde{\psi}_{\lambda_\beta} \rangle \tag{9a}
\]
and
\[
F_{\alpha\beta}(v_1, \tilde{v}_1, \tilde{v}_2) = \langle \psi_{\lambda_0} \mid \tilde{\psi}_{\lambda_\beta} \rangle \langle \psi_{\lambda_\alpha} \mid \tilde{\psi}_{\lambda_\beta} \rangle \tag{9b}
\]
for localized and charge transfer excitations, respectively. The electronic–vibrational excitation energy is expressed in terms of the electronic and vibrational (\( \epsilon_{\lambda_\alpha} \)) energies as
\[
\Delta E_{\lambda_\alpha} = \Delta E_{\varepsilon} + \Delta E_{\nu}, \tag{10}
\]
where
\[
\Delta E_{\varepsilon} = E^*_{\varepsilon} - E_0, \tag{11a}
\]
\[
\Delta E_{\nu} = \sum_{n=0} \left( \epsilon_{\nu_n} - \epsilon_{\nu_0} \right), \tag{11b}
\]
and
\[
\Delta E_{\varepsilon} = E^*_{\varepsilon} - E_0, \tag{11c}
\]
\[
\Delta E_{\nu} = \sum_{n=1} \left( \epsilon_{\nu_n} - \epsilon_{\nu_0} \right), \tag{11d}
\]
for localized and charge transfer processes, respectively. (iii) The Kubo Cumulant expansion \(^{15}\) is then used to express the equilibrium average appearing in Eq. (7) (over the rotational–translational motions of the solvent) in terms of exponential operators involving the equilibrium average of the solute–solvent interaction as well as its fluctuations away from the average.

The result of making these approximations, whose justification and treatment is described in much detail in Refs. 1–3, is to express the band shape function \( I(\omega) \) as a sum of three distinct parts
\[
I(\omega) = I^{(0)}(\omega) + I^{(1)}(\omega) + I^{(2)}(\omega), \tag{12}
\]
which are arranged according to their order in the solute–solvent interaction strength. Each of these three intensity factors contains localized \((r_{00,0})\) and charge-transfer \((r_{00,\alpha})\) electronic dipole matrix elements, involving ground \((0)\) and excited \((\alpha)\) states, relevant F–C factors, and electronic–vibrational energy differences. The higher order terms \(I^{(1)}(\omega)\) and \(I^{(2)}(\omega)\) also contain factors \((h)\) involving the anion–solvent interaction which arise from coupling of the orbitals of the absorbing solute species to those of its neighbors as well as fluctuations \((\delta h \delta h)\) in these so-called resonance integral couplings. The explicit expressions needed to evaluate \(I(\omega)\) are as follows:

\[
I^{(0)}(\omega) = Z^{-1} \sum_{v_1, \tilde{v}_1} \prod_{\nu_0, \lambda_0} \exp\left[ -\beta \epsilon\nu_0(v_1) \right] [F_{\lambda_0}(v_1, \tilde{v}_1)]^2 \sum_{\nu_0, \lambda_0} \exp\left[ -\beta \epsilon\nu_0(v_3) \right] G(\omega, \Delta E_{\varepsilon}, \sigma)
\]
\[
+ Z^{-1} \int \mathcal{D} s(0, \sigma) \sum_{v_1, \tilde{v}_2, \tilde{v}_1} \exp\left[ -\beta \epsilon\nu_0(v_1) \right] [F_{\lambda_0}(v_1, \tilde{v}_1)] [F_{\lambda_0}(v_2, \tilde{v}_2)]^2 \sum_{\nu_0, \lambda_0} \exp\left[ -\beta \epsilon\nu_0(v_3) \right] G(\omega, \Delta E_{\varepsilon}, \sigma), \tag{13}
\]
\[
I^{(1)}(\omega) = Z^{-1} \int \mathcal{D} r(\sigma) \sum_{v_1, \tilde{v}_2, \tilde{v}_1} \exp\left[ -\beta \epsilon\nu_0(v_1) \right] [F_{\lambda_0}(v_1, \tilde{v}_1)]^2 \sum_{\nu_0, \lambda_0} \exp\left[ -\beta \epsilon\nu_0(v_3) \right] G(\omega, \Delta E_{\varepsilon}, \sigma)
\]
\[
\times \langle \frac{-1}{\sigma^2} (\omega - \Delta E_{\varepsilon}) G(\omega, \Delta E_{\varepsilon}, \sigma) + Z^{-1} \int \mathcal{D} r(\sigma) \mathcal{D} s(\sigma) \sum_{\nu, \lambda, \mu, \nu, \lambda} \prod_{\nu_0, \lambda_0} \exp\left[ -\beta \epsilon\nu_0(v_1) \right] [F_{\lambda_0}(v_1, \tilde{v}_1)] [F_{\lambda_0}(v_2, \tilde{v}_2)]^2 \sum_{\nu_0, \lambda_0} \exp\left[ -\beta \epsilon\nu_0(v_3) \right] G(\omega, \Delta E_{\varepsilon}, \sigma)
\]
and

Here, $G(\omega, \Delta E_{ex}, \sigma)$ is a Gaussian function centered at $\Delta E_{ex}$ having a width $\sigma$ which accounts for the inhomogeneous broadening of each vibrational line caused by fluctuations in the solvent's geometry. These Gaussian factors arise in the development of the theory through considerations of fluctuations in the (solvated) electronic energy levels of the solute which arise from fluctuations in the solvent’s instantaneous positions. The resonance integral $\tilde{h}_{R,s,r}$ describes the equilibrium averaged intermolecular resonance couplings [via the electronic Hamiltonian $h(r)$] between the orbitals $\mu$ and $\gamma$, on species located at $R$ and $S$, respectively, whereas $\langle \tilde{h}_{R,s,r} \times \delta \tilde{h}_{R^{'},s^{'},r^{'}} \rangle$ measures correlations between fluctuations in $\tilde{h}_{R,s,r}$ and fluctuations in $\tilde{h}_{R^{'},s^{'},r^{'}}$. The precise physical content of the resonance integrals is given a detailed discussion in Refs. 1 and 2. As will be demonstrated shortly, the full complexity of our expression for $I(\omega)$ given in Eqs. (13)–(15) will not be needed to achieve an interpretation of the two anion spectra treated here. Because the concentration of cyclo-octatetraene and styrene employed in the experiments was quite low, many of the solute–solvent coupling integrals can, as will be demonstrated, be neglected.

Now that we have given a brief overview of the ideas behind our theory, we turn to the task of applying the COT and styrene anions in MTHF glass at 77 K.

III. APPLICATION TO THE COT AND STYRENE SPECTRA

A. Models for anion–solvent interactions

The utilization of an entirely predictive manner of the closed-form expressions for $I(\omega)$ given in Eqs. (13)–(15) requires knowledge of the solvent pair distribution function $p(R, 0)$, the electronic–vibrational energy difference of the absorbing solute, the solute F–C factors, the electric dipole transition integrals $\tilde{r}$, the resonance integrals $\tilde{h}$, and their fluctuations $\langle \delta \tilde{h} \rangle$. Within the presently available experimental data resources, all of this information is certainly not at hand. Hence, our approach will be to employ as much experimental information as is available on the above mentioned factors which relate to the isolated solute species (COT and ST), and to then extract the remaining factors relating to the solute–solvent interaction by fitting the experimental condensed-phase band shape to the functional form for $I(\omega)$ given by our model. It is hoped that, as a result of this process, we may gain important information about both the characteristics of the anion–solvent interactions as well as the strengths and weaknesses of our theory.

1. COT

The nature and relative energies of the low-lying electronic states of COT have been discussed by numerous authors. It is generally considered that the ground state anion is a planar octagonal ($D_{5h}$) species. At this geometry, the π-electron molecular orbitals are of $e_{g}$, $e_{1_u}$, $e_{2_u}$, $e_{2_g}$, and $h_{2_u}$ symmetry, in order of increasing energy. The ground state molecular orbital configuration is $\Psi = a_{g}^{2} e_{1_u}^{4} e_{2_u}^{2} e_{2_g}^{2}$ and three particularly relevant excited configurations have the following orbital occupancies: $\phi_{x}(e_{1_u} - e_{2_u}) = a_{g}^{2} e_{1_u}^{4} e_{2_u}^{2} e_{2_g}^{2}$ $(E_{g})$, $\phi_{y}(e_{1_u} - e_{2_u}) = a_{g}^{2} e_{1_u}^{4} e_{2_u}^{2} e_{2_g}^{2}$ $(E_{g})$, and $\phi_{z}(e_{1_u} - e_{2_u}) = a_{g}^{2} e_{1_u}^{4} e_{2_u}^{2} e_{2_g}^{2}$ $(E_{g})$. Theoretical isolated molecule studies of Carsky et al. and Shida et al. suggest that the transition $E_{g}$ involving the first excited state corresponds to the solution-phase absorption between 350–400 nm being studied in this work. This $E_{g}$ excited state anion state contains appreciable mixing of the configurations $\Psi_{x}(e_{1_u} - e_{2_u}) = a_{g}^{2} e_{1_u}^{4} e_{2_u}^{2} e_{2_g}^{2}$ $(E_{g})$, and $\Psi_{y}(e_{1_u} - e_{2_u}) = a_{g}^{2} e_{1_u}^{4} e_{2_u}^{2} e_{2_g}^{2}$ $(E_{g})$, has an oscillator strength of approximately 0.05, and is believed to be bound in solution. This latter contention is supported by the fact that the band shape corresponding to this transition is rich in vibrational structure. If the $E_{g}$ excited state were autodetaching with a lifetime less than $10^{-15}$ sec, it is highly unlikely that such clear vibrational structure would be seen.

The fine structure in the COT spectrum of MTHF glass at 77 K observed within the 300–400 nm region is found to be uniformly shifted upon changing the nature of the solvent (e.g., in replacing MTHF glass by liquid ammonia). This leads one to conclude that this absorption pattern belongs to a single electronic transition since it is unlikely that such a large change in solvent character would affect two or more excited electronic states by the same manner. From the fact that the spectrum shows relatively sharp vibrational structure in absorption and in emission, Dvorak and Michl concluded that COT is planar and rigid, at least as it exists in the MTHF glass. In addition, the near mirror-image symmetry between the emission and absorption spectra indicates that the rigidity and planarity is preserved in the lowest excited state whose equilibrium geometry differs little from that of the ground state.

The difference between the condensed-phase and gas-phase$^{17}$ excitation energies of COT (transition energies of 324 and 400 nm, respectively) is a measure of the solvent (MTHF) shift which arises because of the differential stabilization of the ground state of COT compared to the lowest excited state of this anion.
Because the concentration of COT in the experiments of Ref. 4 was quite low, there is little interaction between neighbor COT species. Hence, the COT−COT resonance integral couplings can safely be ignored. The lack of low-energy vacant orbitals within the MTHF glass solvent allows us to conclude that COT−to-glass resonance integral interactions may also be neglected.

2. Styrene

The styrene anion in its ground state \( \pi_2^2 \pi_2^2 \pi_3^2 \pi_4^2 \) (\( ^1A'^- \)) is planar and has \( C_{1b} \) (or \( C_2 \)) symmetry, although it is useful to view the anion as having approximate \( C_{2v} \) symmetry. The three lowest energy negative ion excited states correspond to the following orbital excitations: \( \pi_1^1(b_1) - \pi_2^0(\alpha_2) \); \( \pi_1^1(b_2) - \pi_2^0(\alpha_1) \); \( \pi_1^1(b_3) - \pi_2^0(\alpha_3) \) (the symmetry assignments of orbitals in parentheses are with respect to the \( C_{2v} \) group). The semiempirical PPP calculations of Younken et al. yield excitation energy values of 0.7, 1.88, and 3.83 eV for the above excited states, which are in good agreement with the gas-phase experimental values obtained by Jordan et al. from electron transmission spectroscopy (ETS) (0.8, 2.23, and 4.42 eV, respectively). The optical absorption spectrum of \( \text{St}^- \) in MTHF glass at \( 77 \text{K} \) displays strong absorptions at 2.11 and 3.07 eV. That the transition expected near 0.7 eV is not experimentally observed is not surprising since this transition is strongly symmetry forbidden. The observed 2.11 eV transition, which is the subject of study in this paper, occurs at an energy which is near to the above discussed theoretical and gas-phase experimental results. This specific excited state of the \( \text{St}^- \) anion has a lifetime of \( 10^{-12} \text{ sec} \) in the gas phase and is therefore probably several magnitudes longer lived in solution. Thus, it is unlikely that the broadening of this \( \text{St}^- \) absorption due to lifetime effects will be significant in the present work.

As was discussed earlier in reference to COT−, the absence of low-energy empty orbitals in the MTHF glass and the low concentration of styrene used in the condensed-phase experiments allow us to conclude that the “resonance” integral interactions and their fluctuations between \( \text{St}^- \) anion and either the glass or other styrene molecules may safely be neglected, thus permitting the band shape to be described solely by the localized (noncharge transfer) component of \( I^0(\omega) \).

Because both the experimental COT− and \( \text{St}^- \) spectra can most appropriately be analyzed in terms of the localized part of \( I^0(\omega) \), we are able to test our theory in its most rudimentary form (i.e., the form in which it has the fewest adjustable parameters). The results of using our model in these relatively simple cases (i.e., those lacking complicating anion-solute or anion-solvent resonance couplings or charge transfer processes) will provide important insight into the power and/or limitations of our theory.

Having examined the above chemical information concerning the nature of the particular electronic transitions of COT− and \( \text{St}^- \), we now present a brief discussion of some of the computational details which are needed to compute the desired \( I^0(\omega) \). The necessary steps are as follows: (a) We assume that the electronic transitions to be studied are essentially bound-to-bound transitions and that only one bound excited state of the anion is involved. More precisely stated, we assume that the excited anion states studied here are either bound or of sufficiently long lifetime (> \( 10^{-14} \text{ sec} \)) that contributions to the band shape \( B(\omega) \) from the natural lifetime can be ignored. (b) The temperatures of interest are assumed to be low enough so that only the ground vibrational states of the solute species are initially occupied. (c) We assume that the frequencies of the ground and excited electronic state of the anion are similar but that the excited state potential surface is displaced relative to the ground state surface. There is probably little hard evidence to justify this approximation for the case of \( \text{St}^- \), except that the highest occupied orbitals in the ground and excited \( \{ \pi_1^1(b_1) - \pi_2^0(\alpha_1) \} \) states have similar charge density distributions. This approximation is primarily made to permit us to easily calculate the F−C factors. The relaxation of this approximation is not likely to result in a qualitative modification of the computed spectrum. (d) The F−C factors for a given vibrational mode and the corresponding energy differences are assumed to be well approximated within a harmonic oscillator model for which

\[
F_\nu(0,v) = \exp(-X_\nu/2(\nu+1)^{1/2}X_\nu^{1/2})
\]

and

\[
\Delta E_{\nu} = \omega_\nu(\nu+1)
\]

where \( \omega_\nu \) is the vibrational frequency of the participating mode and the mode distortion \( X \) is expressed in terms of the ground-excitated state geometry change \( \Delta R \) and reduced mass \( m \) as \( X = (m\omega_\nu^2/2\hbar) \Delta R^2 \).

After making these approximations, the localized zeroth order band shape function is given by

\[
I^{(0)}(\omega) = R_{30n} \sum \prod \exp(-X_\nu(\nu+1)^{-1}X_\nu^{1/2}G(\omega, \Delta E_{\nu}, \sigma, \sigma)).
\]

The above assumptions are, of course, not generally applicable and for a given system one may be able to more appropriately model each of the various interactions appearing in the general formula shown in Eqs. (14)–(16). However, it is our belief that, given the experimental conditions under which the spectra were taken and the information currently available on the anion states under study, the use of the simple \( I^{(0)}(\omega) \) model together with the above listed simplifications is entirely justified. As we now proceed to use the electronic band shape formula (18) to analyze the COT− and \( \text{St}^- \) spectra, we need to determine values for the quantities \( X_\nu, \omega_\nu, \sigma, \) etc. from the available experimental information. Our procedure will be to vary these quantities in the manner discussed below, to yield optimal agreement between our predicted [via Eq. (18)] spectra and those observed experimentally.

B. Results and discussion

1. COT−

The experimental COT− band shape (see Fig. 1) displays clear vibrational structure corresponding to two superposed vibrational progressions having frequencies
of $\omega_{1s} = 1520 \text{ cm}^{-1}$ and $\omega_{1s} = 720 \text{ cm}^{-1}$. Thus, the seven observed peaks correspond respectively to transitions involving final-state vibrational quantum numbers $(v_1, v_2)$ of $(0, 0), (0, 1), (1, 0) + (0, 2), (1, 1) + (0, 3), (2, 0) + (0, 4), (2, 1) + (0, 5)$, and $(2, 2) + (0, 6)$. Since the second peak is purely due to a $v = 0 \rightarrow v = 1$ excitation of the second vibrational mode, we can determine from the model for the F–C factors given in Eq. (16) that $X_{2s} = 0.683$. A similar analysis of the third peak, which is a superposition of excitations involving both vibrational modes, yields $X_{3s} = 0.590$. The resultant values of $X_{2s} = 0.590$ and $X_{3s} = 0.683$ correspond to changes in geometries which make the most probable “vertical” electronic transition, one which intersects the excited state hypersurface midway between the $v = 0$ and $v = 1$ vibrational levels of both normal coordinates of this state. This is consistent with the conclusions of Dvorak and Michl, who claim that the equilibrium geometry of the excited state involves differs little from that of the ground state. The optimal value of the inhomogeneous broadening factor obtained by fitting Eq. (18) to the experimental spectrum is $\sigma = 0.019 \text{ eV}$, which is considerably smaller than that obtained for the C$_6$H$_6$–I$_2$ charge-transfer spectra in n-heptane liquid at room temperature. This result is consistent with our expectation that the inhomogeneous broadening should be smaller at lower temperatures and in a more rigid medium. The value of the electronic excitation energy of $\Delta E_v = 3.18 \text{ eV}$ obtained from our fit to the experimental data may be compared with the gas-phase value of approximately 3.10 eV obtained by Gygax et al. in their electron-detachment studies. Because of the poor resolution obtained in the gas-phase experiment for this first excited state it is difficult to assign this energy (3.10 eV) unequivocally to the $v = 0 \rightarrow v = 0$ transition. However, should this assignment be made, one may conclude that the ground and the first excited states of COT$^+$ are stabilized by a similar amount by the glassy medium.

Comparison of the predicted and experimentally observed spectra, which are shown together in Fig. 1, reveals that they are in reasonably good agreement except at some of the absorption minima and particularly in the high energy tail. The fact that our F–C envelope with inhomogeneous broadening of each vibronic line matches the overall width of the experimental spectrum is good evidence that the lifetimes of the excited COT$^+$ state is longer than $10^{-14} \text{ sec}$.

Although the calculated spectrum shows small shoulders for the sixth and seventh peaks corresponding to (2, 1) + (0, 5) and (2, 2) + (0, 6) vibrational transitions, respectively, the predicted intensities are not in agreement with experiment. Dvorak and Michl suggest that the intensities of these peaks are due to an additional participating mode of frequency $\omega_{6} = 300 \pm 50 \text{ cm}^{-1}$ whose inclusion would certainly improve the agreement between our prediction and the experimental observations. Even though it is entirely possible that these shoulder peaks arise from additional contributions of a 300 cm$^{-1}$ vibrational mode of COT$^+$, we believe that it is more likely to correspond to an antisymmetric vibrational mode of the ion trio K$^+\text{COT}^+\text{K}^+$ and is not inherently due to the COT$^+$ ion. In support of this argument, we point out that these same shoulder peaks are found to be much less pronounced (as in our predicted spectrum) in the spectra observed by Kimel and Strauss and by Shida and Iwata, whose experiments, even though in different solvents, do not involve the alkali metal cation (M$^+$). Konishi et al. recently observed an ion pair vibration at 142 cm$^{-1}$ in the K$^+\text{Naphthalene}^-$ system in THF solution. By using this observed frequency, we found the ion trio K$^+\text{COT}^+\text{K}^+$ vibration at 249 cm$^{-1}$, which is in reasonably good agreement with the observed frequency of Dvorak and Michl. In the event that our assignment of the low frequency vibrational mode turns out to be experimentally verified, we will be in a good position to conclude that our theory is able to fit the COT$^+$ spectra in solution quite well and thus to provide insights toward understanding condensed phase electronic spectra in terms of inter- and intramolecular interactions.

2. Styrene$^-$

If the slight structure seen near the absorption maximum of $S^-$ is assumed to be vibrational structure, we can assign a frequency of approximately 895 cm$^{-1}$ to the vibrational degree of freedom which seems to couple most strongly to the electronic excitation in the $S^-$ anion. By assuming that the ground electronic state of $S^-$ is vibrationally cold (i.e., has all modes in their $n_v = 0$ states), and considering the nature of the orbital excitation $|\Phi_1(\{b\}) - \Phi_1(\{b\})\rangle$ involved in forming this excited state, one concludes that this active vibration is probably the symmetric carbon–carbon stretching mode shown in Fig. 2(b). The frequency of 895 cm$^{-1}$ is not unreasonable for such a vibration. The extent of the deformation [change in equilibrium geometry between the ground ($\tilde{A}''$) and the excited ($\tilde{A}''$) ion states] is
The optimal electronic excitation energy ($\Delta E_e = 1.85$ eV) obtained by fitting Eq. (18) to the observed spectrum cannot be directly compared with the gas-phase (ETS) value of 2.63 eV because the former contains the effects of solvation on the electronic energy levels of $St^-$ and the latter is not a $\nu = 0 - \nu = 0$ energy difference.

IV. CONCLUSIONS

These results provide substantial evidence that the theory developed in Refs. 1–3 is useful for analyzing the electronic absorption spectra of molecular anions in condensed phases. By comparing the observed COT$^-$ and St$^-$ spectra to the results of Eq. (18), we have gained information about the geometry changes which accompany molecular excitations (via Franck–Condon factors). By examining trends in solvent inhomogeneous broadening, we learn about the strength of the interaction between the solvent and the molecules' electronic states. From the fact that the F–C profile of Eq. (18) is able to account for the entire width of the experimental spectra, we learn that the lifetimes of the excited COT$^-$ and St$^-$ anions are longer than $\sim 10^{14}$ sec in the glassy state (otherwise, lifetime broadening would be required to fit the observed linewidth). Finally, we are able to obtain from our analysis the condensed-phase electronic excitation energies of COT$^-$ and St$^-$ which could be compared with gas-phase excitation energies (were they available) to learn about the differential effects of solvation on the electronic states of these two anions.

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neglected, we performed another set of calculations using localized component of full $I(\omega) = I(0\omega) + I(1\omega) + I(2\omega)$ of Eqs. (13)–(15). This calculation yielded no appreciable changes in the spectrum. The value of optimal ($\Delta R^2$) was found to be of the order of 20 cm$^{-1}$ (small) for COT$^-$ and St$^-$. In particular, for COT$^-$, the nature of the spectrum at the tail end remained unchanged, which further supports our contention that these two shoulder peaks primarily belong to the ion trio K+COT$^-$K$^-$ antisymmetric vibrational mode.