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A Vibronic Model for Infrared Absorption by a Mixed Valence Anion Radical

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Abstract: The radical anion derived from one-electron reduction of the diketone *cis*-10,11-dimethylsuccindan-9,12-dione (I) behaves as a weakly interacting mixed valence compound. The unpaired electron apparently occupies an orbital derived from weak exchange interaction between the two aryl ketone subunits. This paper concerns interpretation of the unusual infrared absorption spectra of this species. These spectra do not include the characteristic absorptions of either structurally related monoketones or monoketyls. A simplified perturbational model is derived to describe vibrational states associated with C-O stretching motions for weakly interacting ketone and ketyl. The frequency and oscillator strength of the relevant transitions are seen to reflect influences of the exchange interaction, V , and a parameter ΔE_0 which represents distortion of the potential energy surface by dissymmetric solvation and ion pairing interactions. The model is reasonably successful in quantitatively accounting for two of the more unusual bands in the spectra and values of V and ΔE_0 are consistent with other properties of the ion. Of particular interest is the conclusion that these transitions are truly vibronic, not simply vibrational, and that similar behavior should be anticipated for other mixed valence compounds.

Introduction

The class of mixed valence compounds presently encompasses a large number of examples representing extraordinarily diverse structural types.^{1-12,18} Their characteristic feature is the presence of an odd electron associated with a pair of atoms or functional groups which are not directly bonded to one another nor are they in conjugation via π bonds. The odd electron may be symmetrically distributed between the two centers or, in the more common situation, it oscillates back and forth between them at a measurable rate. Experimental studies of these species have usually focused on the rate of intramolecular electron transfer and/or on the characteristic electronic charge-transfer transition, or optical intervalence transition

as it is also known. These phenomena have been adequately described in several theoretical discussions.¹³⁻¹⁶

Vibrational spectroscopy, a particularly valuable tool in analyzing other examples of structurally nonrigid molecules, has been largely neglected in the study of mixed valence compounds. In the few instances where experimental attention has been focused on vibrational properties, the analyses were only very qualitative,^{2,12,17} and we know of no previous theoretical efforts in this area. The present paper deals with vibrational properties of a particular organic mixed valence species, the radical anion II derived from one-electron reduction of dione I. The infrared (IR) spectrum of II was investigated under a variety of conditions and a theoretical model was

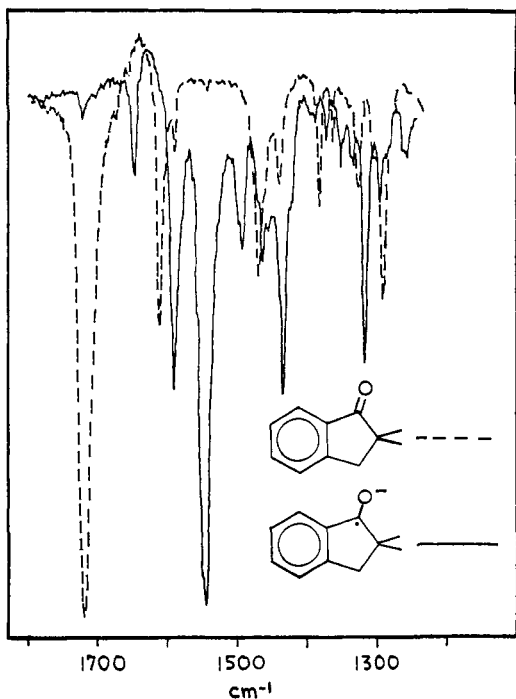
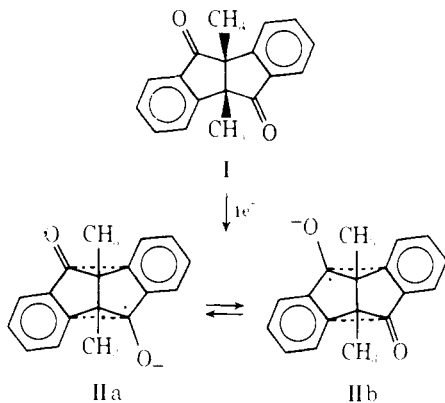


Figure 1. Infrared spectra of 2,2-dimethylindanone (dotted line) and the corresponding ketyl (solid line) in *p*-dioxane-*d*₈. The latter was generated by reduction with potassium metal.

developed which gives a reasonable quantitative account of the more unusual features.



Since a preliminary report on the properties of II,¹² electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) studies carried out in the laboratory of Professor Fabian Gerson at the University of Basel have added several new and important details. The results are fully discussed in a second paper presently in preparation.¹⁹ It will, however, be useful to briefly summarize some of this information before considering the vibrational spectra.

Magnetic resonance spectra of II are quite sensitive to the nature of the solvent and the counterion. Two extremes are exemplified by ether solvents with alkali metal counterions on the one hand, and high dielectric constant solvents with quaternary ammonium ions on the other. Under the former conditions, where strong ion pairing is the rule, hyperfine coupling patterns revealed that spin density was unequally distributed between the two aryl ketone functions. The hyperfines of protons on one ring were significantly greater than those of structurally equivalent protons on the other ring. Nonetheless, the absolute magnitude of the hyperfines was consistent with at least a weak exchange interaction, homoconjugation, between the two π systems. This interaction is represented by the dotted lines in structures IIa and IIb. On the basis of EPR line

widths, the rate of interconversion between IIa and IIb was estimated to be no greater than 10^6 s^{-1} at room temperature for tetrahydrofuran (THF) with K^+ . In high dielectric constant solvents, the situation was exactly reversed. Equal hyperfines were observed for each pair of structurally equivalent protons and the absolute magnitude for any such related pair of protons was equal to the average of the values observed for the K^+ ion pair in THF. This result is equally consistent with a fully symmetric, stationary spin distribution for the ion in high dielectric constant media, or with a very rapid rate of interconversion of IIa and IIb (faster than 10^9 s^{-1} in dimethyl sulfoxide (Me_2SO) at -80°C). Ion pairs may be involved in both situations but their properties are quite different.

Information obtained from the IR studies has proven complementary to the magnetic resonance results. Most simply, IR resolves the ambiguity regarding the situation in high dielectric constant solvents; unsymmetrical structures, IIa and IIb, are uniquely consistent with the results. While the IR spectra are somewhat dependent on the nature of the solution, this phenomenon is not simply related to the solvent dependence of the magnetic resonance spectra. Thus, the latter can be understood on the basis of a classical kinetic model while the former requires a more explicit description of the stationary states of II in solution. A very important result is that certain of the transitions in the IR spectra turn out to be not simply vibrational but rather vibronic, and this peculiarity is directly related to the special properties of mixed valence species.

Results and Discussion

Infrared Spectral Data. It had been shown some years ago by Eargle²⁰ that ketyl radical anions consistently display a strong absorption in the infrared at a frequency roughly 150 cm^{-1} lower than the carbonyl stretching mode for the corresponding ketone. In his experiments the ketyls were generated by alkali metal reduction of the ketone in ether solvents. For our purposes, it was desirable to obtain spectra in dissociating media as well; consequently, two different techniques were utilized. For the ether solvents, tetrahydrofuran (THF) and *p*-dioxane, the ketyls were prepared by contacting solutions of the ketone with a potassium mirror. Spectra were also obtained in solvents of high dielectric constant, Me_2SO and acetonitrile (AN), using a spectroelectrochemical cell. In both cases perdeuterio solvents were employed in order to minimize interfering absorption from C-H bending modes in the region of interest. The spectroelectrochemical technique is particularly convenient since potentiostatic control permits one to obtain spectra of ketone and ketyl at any desired equilibrium concentrations. The alkali metal reductions were usually carried out to a point just shy of complete conversion in order to avoid complications from two-electron reduction. The identity of the reduction product was checked by reoxidation with either O_2 or naphthoquinone to regenerate the original ketone. However, for THF solutions, disproportionation was found to be an important process nonetheless. Thus, when THF solutions of I were titrated with potassium naphthalide, more than 1 equiv was required for complete disappearance of the ketone carbonyl absorption. Because of this complication it was not possible to unambiguously distinguish IR bands of II from those of more highly reduced species in this solvent. Fortunately, the problem did not arise for *p*-dioxane so that it was possible to obtain a spectrum for at least one solvent of low dielectric constant.

Figure 1 illustrates spectra of 2,2-dimethylindanone in dioxane-*d*₈ before and after reduction with a K mirror. The most noteworthy change is disappearance of the carbonyl stretching band at 1710 cm^{-1} for the ketone and the appearance of a new band of comparable intensity at 1548 cm^{-1} in the ketyl. Virtually the same results were obtained with THF-*d*₈ and with $\text{Me}_2\text{SO}-d_6$ or AN-*d*₆ using the electrochemical technique. The

Table I. Carbonyl Stretching Modes of Ketones and Ketyls (cm^{-1})

compd	ketone	ketyl
2,2-dimethylindanone	1710	1548
9-fluorenone	1695	1540
benzophenone ⁷	1668	1562
10-methyldiphen-succindan-9-one	1710	1545

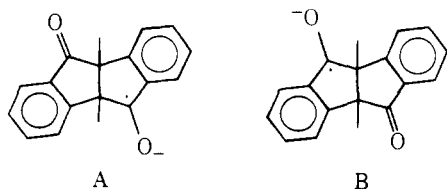
positions of these two bands are only very slightly sensitive to the solvent, always appearing within 5 cm^{-1} of their positions in Figure 1. Table I reports similar data for other simple aryl ketones.

The carbonyl stretching band of I occurs at 1710 cm^{-1} as in other indanone derivatives. The spectrum of the radical anion II was obtained in $\text{Me}_2\text{SO}-d_6$ and $\text{AN}-d_6$ with either KClO_4 or $(\text{CH}_3)_4\text{NPF}_6$ as electrolyte (Figure 2a) and in dioxane- d_8 with K^+ as counterion (Figure 2b). There are no strong absorptions at either 1710 or 1545 cm^{-1} under any of these conditions and the observed bands are abnormally broad (about 60 cm^{-1} at half height). There is no doubt that these spectra represent the radical anion. Using the electrochemical cell isosbestic points were observed when the potential was varied about the first reduction potential and reoxidation provided quantitative regeneration of the dione. Since the second reduction potential is 0.40 V more negative than the first under these conditions, disproportionation to the dianion is not an important factor.

If II were merely a composite of noninteracting ketone and ketyl then one would expect to find bands at both 1710 and 1545 cm^{-1} . On the other extreme, if exchange interactions between the two were sufficiently strong that the minimum energy configuration were actually midway between IIa and IIb then a strong transition at some intermediate frequency should result. The actual spectra correspond to neither of these intuitive expectations. There is only a rather weak band near 1630 cm^{-1} while all of the strong transitions lie below 1510 cm^{-1} . In order to interpret these spectra it is necessary to formulate a description which can accommodate situations intermediate between the two extremes, that is, where the exchange interaction is significant but there remain two minimum energy configurations. The following model incorporates vibrational properties into the same valence-bond type of approach which has been used to describe the electronic properties of mixed valence compounds.^{14,16}

A Vibronic Model for II

It is convenient to begin with a description of an isolated molecule, free of solvation and ion pairing. These effects can be introduced at a later point. As a zeroth-order approximation, we will imagine two valence-bond structures, A and B, for which there is absolutely no exchange interaction between the two aryl ketones. A and B are, in effect, two degenerate ground-state configurations. Ψ_A and Ψ_B are wave functions which describe both electronic and vibrational properties of A and B. They are orthonormal eigenfunctions of some zeroth-order Hamiltonian \mathcal{H}_0 .



$$\Psi_A = \psi_A^{\text{el}} \phi_i(\alpha A) \phi_j(\beta A) \dots$$

$$\Psi_B = \psi_B^{\text{el}} \phi_u(\alpha B) \phi_v(\beta B) \dots \quad (1)$$

ψ_A^{el} and ψ_B^{el} are the electronic terms and the remainder are

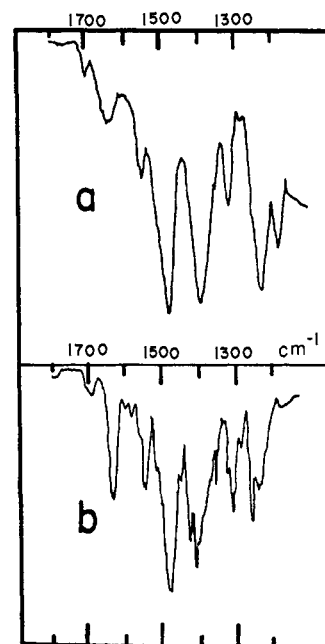


Figure 2. Infrared spectra of the radical anion II in (a) $\text{Me}_2\text{SO}-d_6$ with $(\text{CH}_3)_4\text{N}^+$ as counterion, and (b) p -dioxane- d_8 with K^+ as counterion.

harmonic oscillator functions for each of the normal modes. Thus $\phi_i(\alpha A)$ is the wave function for motion along a normal coordinate α of configuration A in the state with quantum number i , and so on. The eigenvalues corresponding to these states are given by

$$E_{ij}^A \dots = \langle \Psi_A | \mathcal{H}_0 | \Psi_A \rangle = E_0^A + \epsilon_i(\alpha A) + \epsilon_j(\beta A) + \dots \quad (2)$$

$$E_{uv}^B \dots = \langle \Psi_B | \mathcal{H}_0 | \Psi_B \rangle = E_0^B + \epsilon_u(\alpha B) + \epsilon_v(\beta B) + \dots$$

where E_0^A and E_0^B are the potential energies and each additional term represents the contributions of vibrational energy from each normal mode.

These states can serve as a basis set for describing the actual molecule. To this end we now introduce the intramolecular exchange interaction as a perturbation, \mathcal{H}_1 , which mixes the two zeroth-order electronic terms:

$$\langle \psi_A^{\text{el}} | \mathcal{H}_1 | \psi_B^{\text{el}} \rangle = \frac{V}{2} \quad (3)$$

The magnitude of the interaction is expressed by V , which is assumed to be invariant over small displacements along the normal coordinates. The true eigenstates of II, Ψ , may be written as linear combinations of the valence bond functions:

$$\Psi = \psi_A^{\text{el}} \sum_i \sum_j \dots C_{ij} \dots \phi_i(\alpha A) \phi_j(\beta A) \dots$$

$$+ \psi_B^{\text{el}} \sum_u \sum_v \dots C_{uv} \dots \phi_u(\alpha B) \phi_v(\beta B) \dots \quad (4)$$

The coefficients $C_{ij} \dots$ and $C_{uv} \dots$ must be specified for each combination of quantum numbers for the zeroth-order normal modes. The eigenvalues are given by the solution to the Schrödinger equation in the following form:

$$E = \frac{\langle \Psi | \mathcal{H}_0 + \mathcal{H}_1 | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (5)$$

Equation 4 is rather unusual in that it is not a simple product of vibrational and electronic terms. As a consequence, it can turn out that no two eigenstates corresponding to successive quantum levels of Ψ belong to exactly the same electronic manifold. Transitions between such levels would be truly vibronic and not simply vibrational even though they may occur

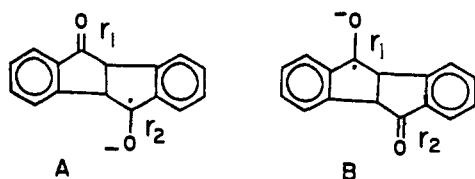
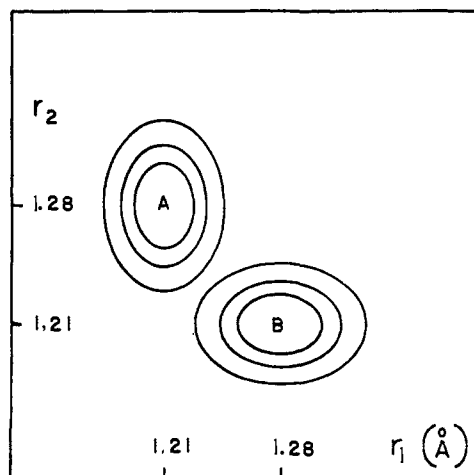


Figure 3. Potential energy surface for valence-bond structures A and B as a function of C–O bond lengths. The ellipses represent equipotential contours with energy decreasing toward the center.

at very low energies. This can have important consequences for the dipole transition moments, a feature which will be elaborated later on. For a specified value of V , application of the variation principle generates a set of secular equations. The solutions to these equations provide the eigenvalues and the coefficients. Much of the tremendous complexity of this problem is due to the large number of normal modes in A and B. In fact it is not necessary to include them all.

Within each of the aryl ketone subunits, certain local vibrational modes will be virtually the same in state A as they are in B. For example, a stretching mode of a particular C–H bond on one of the subunits will not likely be altered by the presence or absence of the odd electron in the neighboring π orbital. Modes of this sort will be termed *independent modes*. Those which are sensitive to the state of oxidation of the subunit will be termed *dependent modes*. The two are explicitly defined as follows:

$$\text{dependent: } \phi_k(\delta A) \neq \phi_s(\delta B)$$

$$\text{independent: } \phi_k(\delta A) = \phi_s(\delta B) \quad \text{for } k = s \quad (6)$$

where δA and δB are a corresponding pair of normal coordinates of A and B.

It can be demonstrated that among the secular equations derived from eq 5, there is a subset which contains only the independent modes and that their solutions, not surprisingly, are identical with the corresponding zeroth-order eigenstates. The remaining subset contains only terms in the dependent modes and only these equations need be explicitly solved. For example, if $\phi(\alpha A)$, $\phi(\beta A)$, $\phi(\alpha B)$, and $\phi(\beta B)$ were the only dependent modes, then the relevant secular equations would be

$$\begin{aligned} C_{ij}(E_{ij}^A - E) + V \sum_u \sum_v C_{uv} S_{ijuv} &= 0 \\ C_{uv}(E_{uv}^B - E) + V \sum_i \sum_j C_{ij} S_{ijuv} &= 0 \end{aligned} \quad (7)$$

where

$$S_{ijuv} = \langle \phi_i(\alpha A) \phi_j(\beta A) | \phi_u(\alpha B) \phi_v(\beta B) \rangle \quad (8)$$

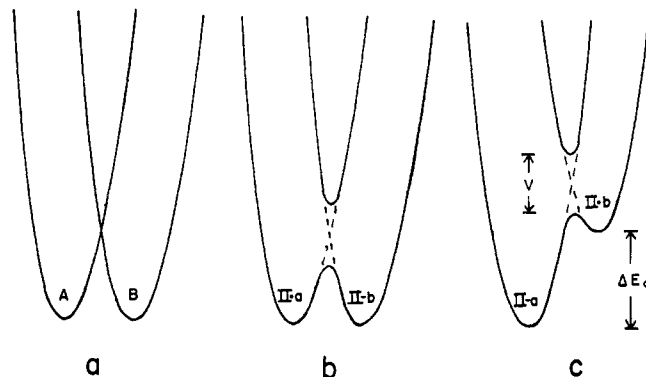


Figure 4. Potential energy profiles along a plane intersecting the two minima of Figure 3. Curve a represents the valence-bond states; b and c show the influence of electronic exchange and dissymmetric solution environment (see text).

Therefore, given a set of vibrational wave functions for the dependent modes of the valence-bond states, one can solve the problem for any particular value of V .

Everything said so far has been quite general and could as well apply to any mixed valence species. In order to actually perform calculations which shed light on the experimental data, it will be very helpful to introduce further simplifying assumptions for the particular case of II. The first assumption will be that the C–O stretching modes are the only dependent modes of A and B. (While it seems reasonable that these modes should be the most sensitive to the oxidation state of the subunits, this assumption is undoubtedly too gross for a refined analysis.) It will further be assumed that the C–O stretching modes are localized and that the corresponding normal coordinates are just the C–O bond lengths themselves, r_1 and r_2 . According to this view, the potential energy surface which describes the motions of the C–O bonds in the two valence-bond states should resemble Figure 3. The two elliptical potential energy wells are centered at the minimum energy configurations of A and B, respectively. The shape and positions of these wells reflect the fact that the C–O bond of the ketyl is slightly weaker and longer than that of the ketone. In fact, the quantitative details of Figure 3 can be obtained empirically from the spectra of model monoketones and monoketyls. Before proceeding it is instructive to note some qualitative conclusions which can be drawn.

So long as A and B are characterized by distinct electronic terms, motions within the two wells will be independent. In regions toward the center of Figure 3, where $r_1 = r_2$, the two surfaces cross one another as illustrated in Figure 4a, but molecules in either state are influenced only by one of the two potential fields. Consequently, motions along the two coordinates will be independent harmonic oscillations with splittings of either 1710 (for r_2 in state A, or r_1 in state B) or 1545 cm^{-1} (r_1 in A, r_2 in B).

The effect of introducing the exchange interaction is to mix the two electronic states. This creates an avoided crossing of the two potential energy surfaces (see Figure 4b). Even if this interaction is weak, the consequences for motions of the C–O bonds are quite important. The most obvious consequence is that the potential surface is no longer a simple quadratic function and that motions along r_1 and r_2 will therefore no longer be simple harmonic oscillations. Nor will motions along the two coordinates be independent of one another. The situation is further complicated by influences of solvation and ion pairing.

Solvation and Ion Pairing

To whatever extent charge distribution in molecules IIa and IIb is dissymmetric, interactions with neighboring counterions

and solvent dipoles will also be dissymmetric in order that the total electrostatic energy is minimized. Stated in another way, a molecule of configuration IIa in its optimum solution environment is more stable than if it adopted configuration IIb in the same environment, and vice versa. This situation is most obvious for ion pairs. For example, alkali metal ions are likely to adopt a position nearest that oxygen atom which bears the most negative charge. Interconversion of IIa and IIb involves relocating these cations.

These effects are averaged out over long time scales by the constant motions of counterions and solvent molecules. However, for time scales short relative to the reorganization process, which requires rotations and translations, IIa and IIb cannot be considered energetically equivalent configurations for a particular molecule. The molecular vibrations probed in our IR studies clearly fall within this time scale. The same considerations apply in analyzing electronic transitions of mixed valence compounds and have received considerable attention for that reason. Marcus¹⁵ and Hush¹⁴ used a dielectronic continuum model to estimate the contribution of solvent to this reorganization energy; however, their approach is inappropriate for situations where ion pairing also plays a role. A purely empirical approach was adopted for the present case.

We denote by ΔE_0 the difference in potential energy of IIa relative to IIb for a state of solvation and ion pairing optimum for only one of the two. This difference will be reflected in Figure 3 as a displacement of one zeroth-order well relative to the other, as illustrated in Figure 4c. Like V , ΔE_0 will enter our calculations of the vibronic states of II as a parameter. The two will be shown to have rather different and distinguishable effects on the calculated transition energies and it is therefore possible to estimate their magnitude through a calculated "best fit" to the experimental data.

There is one final detail implicit in the above model. Namely, it is unlikely that all molecules in a macroscopic sample will be in an identical solution environment at any given instant. Rather there should be some fluctuations in this environment from one molecule to the next and a corresponding fluctuation in ΔE_0 . To the extent that this may result in slightly different vibronic splittings for different molecules, the IR transitions should be inhomogeneously broadened. (Only the dependent modes would be affected.) ΔE_0 is but a small fraction of the total solvation energy of these ions and reflects only a fraction of the total degrees of freedom. Consequently, it is impossible to predict a priori the magnitude or distribution of its fluctuations. It is therefore not likely that experimentally observed line widths will be as diagnostically useful as the frequencies and integrated intensities.

Parameters Used in the Calculations

In order to set up and solve the secular equations for the dependent modes we will need to specify harmonic oscillator functions for each C–O coordinate in both valence-bond states, specifically, $\phi_i(\alpha A)$, $\phi_j(\beta A)$, $\phi_u(\alpha B)$, and $\phi_v(\beta B)$. The required information consists of the force constants, reduced masses, and equilibrium C–O bond lengths.

For the ketone coordinates these were established as follows. The equilibrium C–O bond length was taken to be 1.22 Å, a value characteristic of many aryl ketones as determined by X-ray diffraction.²¹ The force constant and reduced mass were established through isotopic substitution. It was found that the IR absorption observed at 1710 cm⁻¹ for 2,2-dimethylindanone-¹⁶O shifted to 1680 cm⁻¹ for 2,2-dimethylindanone-¹⁸O. (This is the only significant change in the spectrum.) Assuming a simple stretching mode oriented along the bond axis, the reduced masses for the two compounds are given as follows:

$$\mu_{18} = \frac{18m}{18 + m}$$

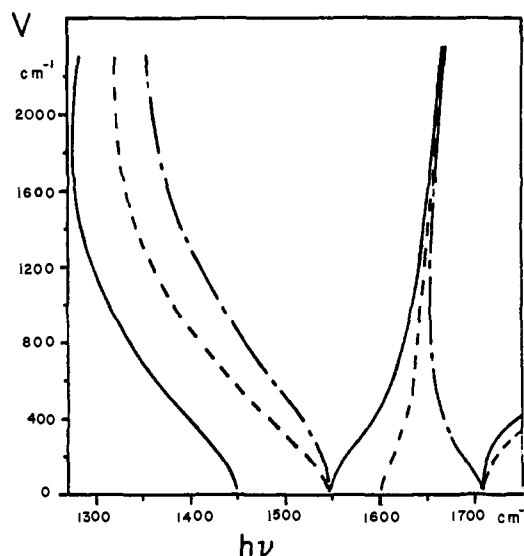


Figure 5. The effect of V on the energies of $0 \rightarrow 1$, $0 \rightarrow 2$, and $0 \rightarrow 3$ transitions calculated for three different values of ΔE_0 : 1450 (solid line), 1600 (dashed line), and 1750 cm⁻¹ (dot-dashed line).

$$\mu_{16} = \frac{16m}{16 + m} \quad (9)$$

where m is the effective mass of the other atoms contributing to the vibration. From this one obtains a value of 5.01 amu for μ and 8.63 mdyn/Å for the force constant of the ¹⁶O ketone.

The situation is less satisfying for the ketyl. The IR band assigned to the C–O stretching mode of 2,2-dimethylindanone anion radical at 1548 cm⁻¹ is only shifted by 10 cm⁻¹ on substitution with ¹⁸O. Furthermore, other bands at lower frequencies are also affected. Clearly the 1548-cm⁻¹ transition is not a pure local C–O stretch. Other vibrations are coupled to it. A rigorous treatment would require inclusion of all such additional vibrations and their couplings in the calculations. There are, unfortunately, too many undefined parameters to permit this approach for the present case. Instead, the simplistic description was retained as an approximation. The reduced mass for the ketyl stretch was taken to be equal to that of the ketone and a force constant of 7.07 mdyn/Å was calculated from the experimentally observed fundamental frequency, 1545 cm⁻¹. The equilibrium C–O bond length in the ketyl was not directly available since no crystal structures have been reported for ketyls. A value of 1.28 Å was adopted as an estimate. This represents the average between typical values for ketones and phenolic types of C–O single bonds,²² and agrees well with the results of INDO calculations on indanone radical anion.

Results of the Calculations

The secular determinant corresponding to eq 7 was generated from a basis set consisting of the first three quantum levels in each of the zeroth-order dependent modes. Overlap integrals (eq 8) were evaluated analytically using a method developed by Band and Freed.²³ The determinant was diagonalized for a series of different values of V and ΔE_0 . Energies for the series of transitions originating from the ground state were then calculated from the eigenvalues.

Figure 5 shows the variations of the $0 \rightarrow 1$, $0 \rightarrow 2$, and $0 \rightarrow 3$ transition energies with V for three different values of ΔE_0 . These two parameters have different effects. For example, increasing V decreases the energy of $0 \rightarrow 1$ but may either increase or decrease the energy of $0 \rightarrow 2$ depending upon the value of ΔE_0 . Increasing ΔE_0 results in a monotonic increase

of all transition energies. As anticipated, for $V = 0$, regardless of the value of ΔE_0 , there are always two transitions predicted at 1710 and 1545 cm^{-1} , respectively. It must be kept in mind that the selection rules for all of these transitions are not the usual $\Delta v = \pm 1$. It is therefore important to be able to calculate the oscillator strength for each transition explicitly, a feature of the problem which is discussed in the next section.

It is difficult to unambiguously identify which of the experimentally observed bands correspond to the transitions of interest. The strong band at about 1480 cm^{-1} seems the most obvious candidate since no other characteristic group vibrations give rise to strong absorptions in this region. Furthermore, it was found that this band could only be satisfactorily assigned to the $0 \rightarrow 1$ transition since alternative assignments never succeeded in providing a strong higher order transition at this frequency for any choice of V and ΔE_0 . (Both this band and that appearing at about 1630 cm^{-1} were affected by ^{18}O , as were other bands in the spectrum.) Finally, the weaker band at about 1630 cm^{-1} could be nicely accommodated as the $0 \rightarrow 2$ transition.

Assuming that these rather tentative assignments are correct, a best fit of the calculated frequencies provides estimates of both ΔE_0 and V . These are $V = 450 \text{ cm}^{-1}$ and $\Delta E_0 = 1620 \text{ cm}^{-1}$ for Me_2SO or AN, and 1640 cm^{-1} for dioxane/ K^+ (see Table II). Note that it is not possible to fit both of these frequencies with very different choices of ΔE_0 and V . As indicated by Figure 5, the effects of varying one of these parameters cannot be compensated by variations in the other. No significant absorptions were detected at the frequencies predicted for higher order transitions, $0 \rightarrow 3$, $0 \rightarrow 4$, etc. The significance of this point rests on the evaluation of the transition moments.

Transition Moments. The transitions of interest involve initial and final states described by eq 4. As commented on earlier, these states may differ in their electronic composition, that is, have different proportions of $\psi_{\text{A}}^{\text{el}}$ and $\psi_{\text{B}}^{\text{el}}$. As a consequence, the transition moments will have contributions from both nuclear and electronic dipole changes. Applying the Born-Oppenheimer principle, the total dipole moment operator can be divided into contributions $m(r)$ for nuclear dipole changes along each normal coordinate r , and a term $m(q, \bar{r})$ for electronic dipole changes corresponding to an average nuclear geometry \bar{r} . It can be shown that the total transition moment is given by eq 10, where the superscripts i and f refer to initial and final states.

$$R_{if} = M^{\text{el}} \sum_i \sum_j \sum_u \sum_v (c_{ij}^i c_{uv}^f - c_{uv}^i c_{ij}^f) S_{ijuv} \\ + M^{\alpha A} \sum_i \sum_j c_{ij}^i c_{i\pm 1j}^f + M^{\beta A} \sum_i \sum_j c_{ij}^i c_{ij\pm 1}^f \\ + M^{\alpha B} \sum_u \sum_v c_{ur}^i c_{u\pm 1v}^f + M^{\beta B} \sum_u \sum_v c_{uv}^i c_{uv\pm 1}^f \quad (10)$$

where

$$M^{\text{el}} = \langle \psi_{\text{A}}^{\text{el}} | m(q, \bar{r}) | \psi_{\text{B}}^{\text{el}} \rangle \\ M^{\alpha A} = \langle \psi_i(\alpha A) | m(\alpha A) | \phi_{i\pm 1}(\alpha A) \rangle$$

etc.

The vibrational terms, $M^{\alpha A}$, $M^{\beta A}$, can each be evaluated empirically from the integrated intensities of C-O stretching bands in the IR spectra of 2,2-dimethylindanone and its radical anion. There is no similarly straightforward method for estimating M^{el} . That it does indeed play a role was indicated by the following exercise. First, oscillator strengths for the various transitions were calculated from vibrational terms alone (M^{el} was set equal to zero in eq 10). The results are reported in Table II, column 4. This calculation badly underestimates the intensities of both $0 \rightarrow 1$ and $0 \rightarrow 2$ transitions (the latter is predicted to be forbidden), and overestimates the intensity of

the $0 \rightarrow 3$ transition which is not observed. Calculations were then repeated including a finite value of M^{el} oriented along a line joining the two carbonyl carbons. By adjusting the scalar magnitude of M^{el} to a value roughly twice that of the vibrational terms, results reported in the last column of Table II were obtained. The first three transitions are now fit rather well, although serious discrepancies are encountered for some of the higher order transitions. A more refined estimate of M^{el} hardly seems worthwhile in view of the errors resulting from our other approximations.

Summary and Conclusions

The chief oversimplification in this analysis has been the neglect of dependent modes other than the C-O stretches. Each dependent mode interacts with all other dependent modes under the influence of \mathcal{H}_1 , and consequently neglect of any of them must always result in some systematic errors. Furthermore, in the present instance, it is certain that there are other dependent modes, for example, those which are coupled to the C-O stretching band in the ketyl. (These may be responsible for the other anomalously strong bands in the IR spectra of II at frequencies below 1400 cm^{-1} .) The assignments in Table II can be regarded as approximations at best. However, we believe that the general agreement between calculated and experimental results is not simply circumstantial. In particular it is encouraging that the derived values of V and ΔE_0 are in good accord with results of the magnetic resonance studies.

For the ion pairs in ether solvents the hyperfines of protons on the aromatic rings reflect a spin distribution corresponding to weak interaction between the two π systems. Gerson and Ohya-Nishiguchi obtained good agreement from a HMO calculation in which the homoconjugative resonance integral was 0.05β for each transannular interaction,¹⁹ where β is the normal resonance integral for a C-C π -bond (about 18 kcal/mol). In terms of a perturbational MO description, this would correspond to $V = 214 \text{ cm}^{-1}$, in rather good agreement with our value of 450 cm^{-1} .

The parameter ΔE_0 is of some relevance to the kinetics of interconversion between IIa and IIb. According to kinetic models based on dielectric continuum description of solvation, ΔE_0 should represent roughly twice the activation energy for this process. (At the midpoint of the reaction, the solvation sphere is symmetrical and the electrostatic energy is calculated to be midway between the two extremes.) In high dielectric constant solvents the rate must be faster than 10^9 s^{-1} to account for the fully averaged spin distribution. For an activation energy of 810 cm^{-1} (one-half of ΔE_0 in these solvents) and a normal unimolecular preexponential the predicted rate is about 10^{11} s^{-1} at 273 K. The situation for the ion pairs is substantially different. In dioxane, the rate must be less than 10^6 s^{-1} since the EPR spectrum corresponds to an unsymmetrical spin distribution. Yet the IR studies indicate that ΔE_0 is only slightly greater (1640 cm^{-1}) than in the high dielectric solvents. In this instance we are dealing with interconversion of ion pairs. The kinetics can no longer be treated in terms of usual Marcus or Hush theory. Thus, it is likely that the cation is closely associated with one of the two O atoms and that the interconversion requires at least partial dissociation of the ionic partners. The electrostatic energy for this process will depend upon the path followed by the cation in getting from one O atom to the other, and this may well exceed ΔE_0 .

Despite the considerable uncertainties, these studies have provided insight into the structure of II and its interaction with the solution. Furthermore, it is almost certain that vibronic transitions will play an important role in IR and Raman spectra of other mixed valence species. The difficulty lies in identifying and assigning these bands among the usually complex manifold of conventional transitions. In favorable cases where all of the dependent modes can be well characterized, it is to be expected

Table II. Infrared Vibronic Transitions for the Radical Anion II

assignment ^a		transition energy, cm ⁻¹		integrated intensity ^b		
		obsd	calcd	obsd	calcd-1	calcd-2 ^c
0 → 1	Me ₂ SO or AN	1480	1480	100	32	88
	dioxane/K ⁺	1485	1490	60	38	86
0 → 2	Me ₂ SO or AN	1638	1635	18	3	17
	dioxane/K ⁺	1640	1643	20	3	22
0 → 3	Me ₂ SO or AN		1794	n.d. ^d	42	6
	dioxane/K ⁺		1806	n.d.	39	4
0 → 4	Me ₂ SO or AN		3058	n.d.	0.0	0.5
	dioxane/K ⁺		3063	n.d.	0.0	0.0
0 → 5	Me ₂ SO or AN		3160	n.d.	0.0	42
	dioxane/K ⁺		3182	n.d.	0.0	42
0 → 6	Me ₂ SO or AN		3266	n.d.	0.0	0.5
	dioxane/K ⁺		3270	n.d.	0.0	2
0 → 7	Me ₂ SO or AN		3381	n.d.	0.0	69
	dioxane/K ⁺		3400	n.d.	0.0	72

^a Calculations were carried out with $\Delta E_0 = 1620 \text{ cm}^{-1}$ for Me₂SO, 1650 cm^{-1} for dioxane/K⁺. V was fixed at 450 cm^{-1} . ^b Integrated intensities are given in arbitrary units relative to the strongest band observed (1480 cm^{-1} in Me₂SO). ^c Calcd-1 reflects intensities calculated with $M_1^{\text{el}} = 0$. For calcd-2 M_1^{el} was fixed at a value roughly twice that of M_1^{r} for the ketone stretching mode (see text). ^d n.d. indicates that no signal was detected at or near the relevant frequency.

that analyses of the sort presented here will provide detailed and precise information unavailable from other spectroscopic methods.

Experimental Section

All IR spectra were recorded on a Perkin-Elmer Model 283 IR spectrometer. A Princeton Applied Research Model 173 potentiostat/galvanostat was used for all cyclic voltammetry and controlled potential electrolysis experiments. Microanalyses were carried out by Galbraith Laboratories, Inc. ¹H NMR spectra were recorded on a Bruker HX-270 spectrometer.

Electrochemical Reductions. The IR transparent electrochemical cell used was a modified version of that described by Heineman, Burnett, and Murray.²⁴ An 80-mesh platinum grid working electrode surrounded by a platinum grid auxiliary was sandwiched between two CaF₂ plates with a 0.10-mm Teflon spacer. An Ag/AgCl reference electrode protruded through one of the fill holes in the CaF₂ window. Good potential control was achieved with Nernstian equilibrium established within 3 min of commencing electrolysis. Commercial acetonitrile was distilled from KMnO₄/Na₂CO₃ and again from CaH₂ prior to use. Acetonitrile-*d*₃ was dried over activated alumina. Me₂SO and Me₂SO-*d*₆ were distilled from KOH and stored over 4 Å molecular sieves. Commercial potassium perchlorate was dried and stored in a vacuum oven. Tetramethylammonium hexafluorophosphate was prepared from tetramethylammonium iodide and ammonium hexafluorophosphate, recrystallized from ethyl acetate, and dried under vacuum. In a typical experiment 10 mL of a solution 0.04 M in ketone and 0.4 M in electrolyte was prepared, bubbled with N₂ to remove oxygen, and syringed into the cell.

Chemical Reductions. The vacuum cell used for chemical reductions is essentially the same as that described by Eargle.²⁰ Commercial dioxane-*d*₈ was distilled from NaH, and THF-*d*₈ was distilled from NaH, then LiAlH₄; both were stored on the vacuum line over Na/K alloy and degassed with several freeze-pump-thaw cycles prior to use.

2,2-Dimethylindanone. 1-Indanone (2.50 g) was added to 1 equiv of 0.3 M THF solution of lithium diisopropylamide (LDA) under nitrogen at $-78 \text{ }^\circ\text{C}$, and the solution stirred for 0.5 h. One equivalent of methyl iodide was added, the temperature was lowered to $-78 \text{ }^\circ\text{C}$, and a second equivalent of LDA and methyl iodide were added in a similar manner. The mixture was stirred for 2 h at $25 \text{ }^\circ\text{C}$, neutralized, and extracted with ether to yield 2.57 g of crude product, 95% pure by VPC (20M Carbowax). The crude product was purified by preparative VPC to yield a colorless solid: mp $43\text{--}44 \text{ }^\circ\text{C}$; IR (CHCl₃) 2950, 2910, 1710, 1610, 1468, 1290, 990 cm⁻¹; NMR (CCl₄) δ 1.21 (s, 6), 2.97 (s, 2), 7.33 (d, 2), 7.50 (t, 1), 7.69 (d, 1). Anal. Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.66; H, 7.64.

cis-10,11-Dimethyldiphensuccindan-9,12-dione. 1, 2,3-Diphenylsuccinonitrile was prepared and hydrolyzed by the method of Wawzonek^{25,26} to yield a mixture of *meso*- and *dl*-2,3-diphenylsuc-

cinic acids,²⁷ mp $218\text{--}230 \text{ }^\circ\text{C}$. This acid mixture (10.0 g) was treated with 60 mL of concentrated H₂SO₄ and 1 mL of fuming H₂SO₄ at $75 \text{ }^\circ\text{C}$ for 0.5 h and poured over ice water, and the resulting precipitate recrystallized from ethanol to yield 3.90 g of diphensuccindan-9,12-dione,²⁸ mp $202\text{--}204 \text{ }^\circ\text{C}$. This diketone (2.50 g) and 3 equiv of potassium hydroxide in 150 mL of ethanol were stirred with 1.5 mL of methyl iodide for 1 h at room temperature and 30 min at $40 \text{ }^\circ\text{C}$. Standard workup yielded 2.47 g of 10-methyldiphensuccindan-9,12-dione as a viscous oil: IR (CHCl₃) 3075, 2985, 2965, 2885, 1713, 1600, 1465, 1285, 1102, 970 cm⁻¹; NMR (CDCl₃) δ 1.77 (s, 3), 4.07 (s, 1), 7.43 (m, 2), 7.68 (m, 4), 7.88 (t, 2). This material (1.0 g) was methylated using the procedure outlined above in the preparation of 2,2-dimethylindanone. The resulting solid was recrystallized from ethanol to yield 0.50 g of *cis*-10,11-dimethyldiphensuccindan-9,12-dione: mp $126\text{--}128 \text{ }^\circ\text{C}$; IR (CHCl₃) 3070, 2880, 2835, 1710, 1596, 1463, 1287, 965 cm⁻¹; NMR (CDCl₃) δ 1.62 (s, 6), 7.36 (t, 1), 7.58 (m, 2), 7.76 (d, 1). Anal. Calcd for C₁₈H₁₄O₂: C, 82.42; H, 5.38. Found: C, 82.22; H, 5.34. The assignment of *cis* configuration was verified by comparison with an authentic sample prepared by the alternative route described below.

2, 2,3-Diphenylsuccinonitrile²⁵ (2.0 g) was methylated twice using the procedure described above in the preparation of 2,3-dimethylindanone and purified by preparative TLC to yield 0.965 g of *dl*-2,3-dimethyl-2,3-diphenylsuccinonitrile,²⁹ mp $147\text{--}148 \text{ }^\circ\text{C}$. This dinitrile (0.092 g) was hydrolyzed with a mixture of 0.4 mL H₂O, 0.4 mL of concentrated H₂SO₄, and 0.2 mL of glacial acetic acid to yield 0.083 g of a cyclic anhydride: mp $158\text{--}159 \text{ }^\circ\text{C}$; NMR (CDCl₃) δ 1.37 (s, 6), 7.21 (m, 4), 7.40 (m, 6). The melting point, which matches that previously reported³⁰ by workers who resolved the optical isomers, unambiguously identifies this material as *dl*-1,2-dimethyl-1,2-diphenylsuccinic anhydride. This *dl* anhydride was cyclized with concentrated H₂SO₄ using the same procedure described above for the cyclization of the 2,3-diphenylsuccinic acids. The resulting *cis*-10,11-dimethyldiphensuccindan-9,12-dione had melting point and spectral properties identical with those of the material prepared by the first route.

10-Methyldiphensuccindan-9-one. 10-Methyldiphensuccindan-9,12-dione (1.50 g) in 2.0 mL of 1,3-propanedithiol was stirred with 1 equiv of boron trifluoride diethyl etherate for 45 min at room temperature and 5 min at $40 \text{ }^\circ\text{C}$. Standard workup gave a white solid which was recrystallized from diethyl ether to yield 1.44 g of the corresponding 12-dithioketal of the starting diketone: mp $168\text{--}171 \text{ }^\circ\text{C}$; IR (CHCl₃) 3076, 3000, 2980, 2910, 1713, 1605, 1472, 1370, 1290, 971 cm⁻¹; NMR (CDCl₃) δ 1.88 (s, 3), 2.1–2.4 (m, 2), 3.0–3.4 (m, 4), 4.37 (s, 1), 7.26 (m, 2), 7.39 (t, 1), 7.50 (m, 2), 7.63 (t, 1), 7.72 (d, 1), 7.92 (d, 1). This dithioketal (0.05 g) was selectively reduced by treatment with an excess of Raney nickel³¹ in ethanol at $25 \text{ }^\circ\text{C}$ for 2 h to yield 0.03 g of 10-methyldiphensuccindan-9-one as a viscous oil: IR (CHCl₃) 3070, 2915, 1710, 1607, 1478, 1458, 1287, 972, 962 cm⁻¹; NMR (CDCl₃) δ 1.61 (s, 3), 3.18 (d, 1), 3.72 (m, 2), 7.1–7.75 (m, 6).

2,2-Dimethylindanone-¹⁸O. 2,2-Dimethylindanone (0.11 g) in 5.0 mL of aniline was refluxed for 12 h with 0.20 mL of BF₃·Et₂O. The resulting crude solid was recrystallized from ether to yield 0.08 g of 2,2-dimethylindan-1-phenylimine: mp 43–46 °C; IR (CHCl₃) 2960, 2930, 1658, 1592, 1483, 1464, 1301, 1165, 1005, 996 cm⁻¹; NMR (CDCl₃) δ 1.37 (s, 6), 2.99 (s, 2), 6.50 (d, 2), 6.85 (m, 3), 7.10 (t, 1), 7.30 (m, 4). This phenylimine (0.0543 g) and 0.01 mL of 99% H₂¹⁸O were treated with dry HCl until the solid began to go into solution and heated in a 130 °C oil bath for 0.5 h. The solution was extracted with a 1:1 mixture of cyclohexane–chloroform and the solvents were removed under vacuum to yield 0.0375 g of 2,2-dimethylindanone-¹⁸O; IR (CHCl₃) 1675, 1608, 1290, 990 cm⁻¹.

Note Added in Proof. Since the present manuscript was accepted, very closely related theoretical studies were reported by S. B. Piepho, E. R. Krausz, and P. N. Schatz (*J. Am. Chem. Soc.*, **100**, 2996 (1978)). These authors have applied the same sort of approach to describing vibronic structure of the optical intervalence transition for the special case of only one dependent coordinate.

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Fragmentations of Alkane Molecular Ions

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Abstract: The appearance energies of daughter ions for the major fragmentations of butane and methylpropane and those for loss of CH₃⁺ and CH₄ from propane, pentane, methylbutane, and hexane have been measured. These reactions for molecular ions of low internal energy content (rate constants in the range 10⁵–10⁷ s⁻¹) have been investigated by measurements of the relative abundances of metastable peaks and their accompanying translational energy releases. The deuterium-labeled species propane-2,2-²H₂, butane-1,1,1,4,4,4-²H₆, butane-2,2,3,3-²H₄, butane-1,1,1,2,2-²H₅, and methyl-²H₃-propane-2-²H₁ have also been examined. The accumulated information for loss of methyl from straight-chain alkane molecular ions indicates that this reaction proceeds largely by loss of a terminal methyl group, accompanied by a concerted H atom shift to yield a secondary carbonium ion. Loss of methyl from within the hydrocarbon chain may proceed from a molecular ion which has isomerized to a methyl-branched alkane or by a concerted extrusion of methylene together with an adjacent H atom, again producing a secondary carbonium ion. Hydrogen atoms are not "scrambled" in either of these processes. It is proposed that the eliminations of methane from metastable molecular ions of butane and methylpropane both yield [cyclopropane]⁺ as the daughter ion. The losses of CH₄, CH₃D, and CD₃H (metastable peak abundance ratios 26:15:10) from butane-2,2,3,3-²H₄ were significantly different from those for the tetradeuterated isomer, methyl-²H₃-propane-2-²H₁, where the ratios 78:18:~1 were observed. These results are compatible with the retention of skeletal structure in the linear alkane molecular ions. However, the metastable molecular ions of butane have a higher energy content than those of methylpropane and so isomerization of the former to the latter prior to fragmentation cannot be ruled out.

Introduction

In 1945 Hipple, Fox, and Condon examined the normal mass spectrum of butane¹ and observed diffuse peaks therein; these they interpreted as arising from decompositions of ions in the field-free region preceding the analyzer (the magnet). Since then there have been many investigations directed toward identifying the decomposition mechanisms of the butane molecular ion and of alkane molecular ions in general.^{2,3}

A 1973 review² states that alkane molecular ions inter alia decompose via rearrangements, which possibly are accompa-

nied or preceded by partial or complete loss of the positional identity of the hydrogen atoms—a well-established feature of the chemistry of alkene molecular ions and alkyl cations.³ However, a survey of the recent literature (cf. ref 3) reveals that it remains to be established whether alkane molecular ions isomerize prior to decomposition, rearrange during decomposition, or indeed whether H atoms do lose their positional identity prior to fragmentation (for detailed discussion cf. ref 4–7). Many techniques, including isotopic labeling, have been used to interpret the mass spectra of the simplest class of or-