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ARTICLES

Nanosecond Time-Resolved Infrared Studies of Visnagin and Khellin Triplets and Radical Ions

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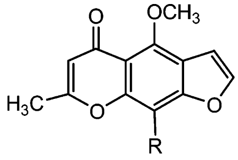
Time-resolved infrared spectroscopy (TRIR) and density functional theory (DFT) calculations were used to directly observe and assign the vibrational spectra of the triplet states of visnagin and khellin, and to investigate their electron-transfer chemistry. The TRIR spectra of triplet visnagin and triplet khellin, and of their radical cations and anions, were obtained upon 266 nm laser flash photolysis in acetonitrile and in deuterated acetonitrile. The radical cations were observed in the presence of chloranil, and the radical anions were formed in the presence of NaI and KSCN. The TRIR spectra are in good agreement with the calculated vibrational spectra. We did not observe the related neutral radicals by TRIR spectroscopy upon laser flash photolysis (LFP) of khellin in the presence of hydroquinone, but we found evidence for the formation of semiquinone and neutral visnagin radicals upon LFP of visnagin and hydroquinone.

I. Introduction

Khellin **1** and visnagin **2** are furanochromones extracted from the seeds of *Ammi visnaga* (Arabic *khella*), a plant common in the Eastern Mediterranean region.[1,2] In 1982 Abdel-Fattah et al. reported encouraging results from the application of a new method for the treatment of skin diseases, such as vitiligo, combining orally administered khellin and solar irradiation.[3] More detailed studies of khellin's properties confirm that it has several advantages compared with psoralens used classically for this purpose. Psoralens (furocoumarins) are a class of photomutagenic and photochemotherapeutic molecules that covalently modify nucleic acids. This is generally believed to proceed by intercalation of the psoralen between adjacent base pairs in the DNA duplex followed by two successive photocycloaddition reactions that cross-link the two DNA strands.[4−6]



Khellin **1** R = OCH_3
Visnagin **2** R = H

Khellin and visnagin, whose chemical structures closely resemble that of psoralen, sensitize similar photobiological, photochemical, and phototherapeutic effects but are less phototoxic and carcinogenic presumably because they predominantly form monoadducts upon photolysis rather than cross-links.[4]

Khellin, when combined with artificial ultraviolet (UVA) or solar irradiation (KUVA), is reported to repigment the skin of individuals suffering from vitiligo as effectively as PUVA photochemotherapy.[3] Khellin may be used topically to avoid systemic side effects. The exact mechanism of KUVA-induced repigmentation is not known. However, it has been recently reported that khellin activated by UVA stimulates melanocyte proliferation and melanogenesis.[4]

Although PUVA therapy has been in use for over 20 years and is the most widely employed photochemotherapy treatment in dermatology, the molecular mechanisms by which it clears skin disorders have not been adequately elucidated. Considerable research efforts have been directed toward identifying the excited-state intermediates involved in the photocycloaddition chemistry of psoralens that are used in PUVA therapy.[5−9] Most of the photochemistry of psoralens and nucleic acid bases proceeds from singlet excited states, but there is evidence in the literature that indicates that the triplet excited states of nucleic acids and psoralens also play important and relevant roles in the observed photochemistry.[10,11] In the case of psoralens, it has been shown that psoralen triplet excited states are effectively quenched by nucleic acid bases[11] and the formation of psoralen−pyrimidine base adducts was found to be quenched by oxygen and paramagnetic ions, which are very efficient triplet-state quenchers.[12]

In this study, we have investigated the vibrational spectra of the triplet-excited states of khellin and visnagin using time-resolved infrared (TRIR) spectroscopy. We have assigned vibrational bands of transient intermediates involved in their photochemistry with the aid of computational methods. In additon to the triplet excited states, we examined the related radical cations and radical anions of visnagin and khellin. The vibrational frequencies of each intermediate were obtained at the B3LYP/6-31G** level with the optimized B3LYP/6-31G* geometry.[14,15] Calculations were performed in the gas phase as well as in acetonitrile solution using the PCM[15,16] solvation model on the optimized B3LYP/6-31G* geometry. As part of our general interest in elucidating the role of electron transfer in psoralen photochemistry, we observed the formation of the radical anions of khellin and visnagin upon 266 nm laser flash

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photolysis (LFP) in the presence of electron donors such as NaI or KSCN. Although the assignment of the radical anion peaks was difficult due to overlapping of the transient absorption spectra of their triplets and radical anions, major peaks were successfully attributed to the radical anions of **1** and **2** at 1561 and 1594 cm^{-1}, respectively. We did observe the formation of the radical cations of both compounds and the visnagin neutral radical, in the presence of chloranil and hydroquinone.

II. Experimental Section

Materials. Khellin **1** (269.25 g/mol, Lot No. GA16976), visnagin **2** (230.22 g/mol, Lot No. 01412CT), tetrachloro-1,4-benzoquinone (chloranil, 245.88 g/mol, Lot No. 17727BB), potassium thiocyanate (81.07 g/mol, Lot No. 16104D4), acetonitrile, and deuterated acetonitrile were purchased from Sigma-Aldrich (St. Louis, MO) with purity >99% (HPLC). Hydroquinone (110.11 g/mol) was purchased from Eastman Organic Chemicals (Rochester, NY). Sodium iodide (149.89 g/mol, Lot No. B26333) was purchased from Baker (Philipsburg, NJ) with a purity of 99% (HPLC). All the chemicals were used as received.

Time-Resolved Infrared (TRIR) Spectroscopy Studies. TRIR experiments were conducted with a JASCO TRIR-1000 dispersive-type IR spectrometer with 16 cm^{-1} resolution following the method described in the literature.[13]

Each sample solution was prepared with an optical density of 0.6−1.0 with a 0.5 mm path length. A total volume of 10−20 mL of the deoxygenated sample solution was continuously circulated between two calcium fluoride salt plates. The sample was excited by 266 nm laser pulses of a Nd:YAG laser (50 Hz repetition rate, 0.6−0.8 mJ/pulse power), which is crossed with the broad-band output of a $MoSi_2$ IR source (JASCO); the IR monochromator is located after the sample and the intensity change of the IR light induced by photoexcitation is monitored as a function of time by an MCT photovoltaic IR detector (Kolmar Technologies, KMPV11-1-J1) with a 50-ns rise time, amplified with a low-noise NF Electronic Instruments 5307 differential amplifier and digitized with a Tektronix TDS784D oscilloscope. The TRIR spectrum is analyzed by the IGOR PRO program (Wavemetrics Inc.) in the form of a difference spectrum:

$$\Delta(A_t) - \log(1 + \Delta I_t/I)$$

where ΔI_t is the intensity change induced by photoreaction at time t and I is the IR intensity for the sample without photoexcitation. Thus, the depletion of reactant and the formation of transient intermediates or products lead to negative and positive signals, respectively.

Density Functional Calculations. All calculations were performed using Gaussian 98[15] on the Linux Cluster at the Ohio Supercomputer Center. All geometries were optimized at the B3LYP/6-31G* level of theory (unrestricted B3LYP was used for the open-shell systems), and single-point energies were also obtained at the B3LYP/6-31+G** level with the optimized B3LYP/6-31G* geometry.[15,16] Stationary points were verified to be energy minima via vibrational frequency analyses (B3LYP/6-31G*) in which all the calculated vibrational frequencies were nonimaginary. Zero-point vibrational energy (ZPE) corrections were also obtained by vibrational frequency calculations. For the vibrational spectra, vibrational frequencies were scaled by 0.9613.[15] Spin contamination for the optimized structures were low: $0.75 < \langle S^2 \rangle < 0.79$ for the doublet states and $2.0 < \langle S^2 \rangle < 2.1$ for the triplet states. Simulated (vertical) UV spectra were calculated using time-dependent density functional theory (TD-DFT) with the B3LYP/6-31+G** level at the minimized B3LYP/6-31G* geometry for each structure.[15,16] The self-consistent reaction field with polarizable continuum model (PCM) was applied to the calculation of solution structure and energies.

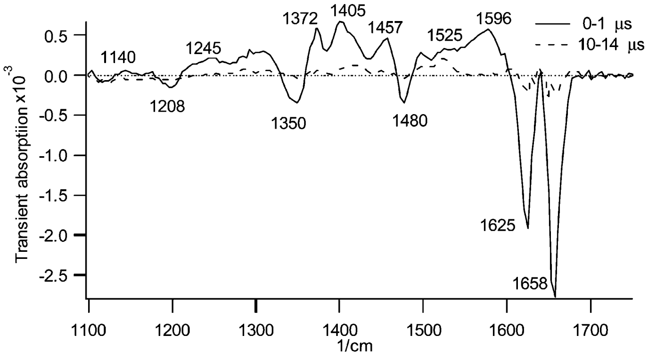


Figure 1. Transient IR spectra produced upon LFP (266 nm) of 6 mM **1** in argon-saturated acetonitrile (1100−1300 and 1600−1750 cm^{-1}) and in deuterated acetonitrile (1300−1600 cm^{-1}).

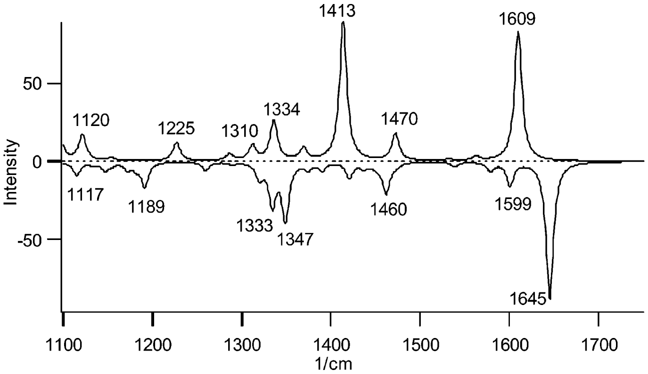


Figure 2. Calculated IR spectra of **1** (down) and ^{3}**1*** (up) in acetonitrile.

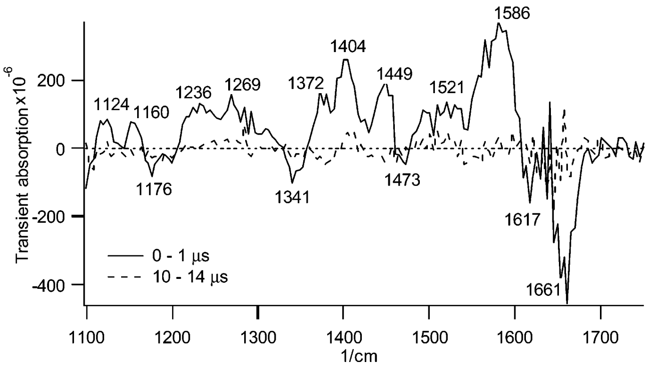


Figure 3. Transient IR spectra produced upon LFP (266 nm) of 10 mM visnagin (**2**) in argon-saturated acetonitrile (1100−1300 and 1600−1750 cm^{-1}) and in deuterated acetonitrile (1300−1600 cm^{-1}). **2** (down) and ^{3}**2*** (up).

III. Results and Discussion

Laser flash photolysis (266 nm, 0.5−0.7 mJ/pulse, 50 Hz repetition) of khellin (**1**) and visnagin (**2**) in argon-saturated acetonitrile or acetonitrile-d_3 produced the transient spectra of ^{3}**1*** and ^{3}**2*** (Figures 1 and 3). The negative peaks are due to depletion of the ground states of **1** and **2**, and the positive peaks are due to the presence of a transient intermediate. TRIR spectra were most often recorded in acetonitrile. Acetonitrile obscures the IR region between 1300 and 1600 cm^{-1}; therefore, this

TABLE 1: Experimental and Calculated Frequencies for Khellin Ground State 1, ^{3}1*, $1^{\bullet -}$, $1^{\bullet +}$, and 1H$^\bullet$, and Chloranil Ground State, Its Triplet, and Its Radical Anion

species	observed bands[a] (cm^{-1})	DFT-predicted bands[b] (cm^{-1})	DFT-predicted rel intensities[c]	mode
1	1658	1645	87.3	C═O stretching
	1625	1599	14.0	pyrone C═C stretching
	1480	1460	17.3	furan C═C stretching
	1350	1347	38.1	C−O stretching, C−H bending
^{3}**1***	1596	1609	81.7	pyrone C═C stretching
	1525	1470	17.5	C═O stretching
	1457	1413	88.2	furan C═C stretching
	1405	1334	24.6	phenyl C═C stretching
	1372	1310	8.6	C−O stretching
	1245	1225	11.6	C−H bending
$\mathbf{1}^{\bullet -}$	1561	1566	80.4	C═O stretching
$\mathbf{1}^{\bullet +}$	1136	1128	36.5	pyrone C−O stretching
1H$^\bullet$		1425	15.0	O−H bending
		1378	11.6	C═C stretching
		1291	9.8	C−C−C bending
		1190	7.8	C−H bending
chloranil	1693	1701	58.7	C═C symmetric stretching
	1569	1551	28.9	C═C asymmetric stretching
	1232	1196	13.6	C−C−C deformation
^{3}**chloranil***	1550	1586	25.4	C═O asymmetric stretching
	1525	1502	40.5	C═O symmetric stretching
	1206	1204	84.6	C═C asymmetric stretching
	1156	1154	32.7	C−C symmetric stretching
chloranil$^{\bullet -}$	1653, 1606, 1525	1586	51.4	C═O stretching
	1144	1147	39.6	C−C symmetric stretching

[a] TRIR. [b] B3LYP calculations with the 6-31G* basis set after scaling by a factor of 0.9613. [c] The largest calculated peak in the spectrum is defined as 100%.

spectral region was studied in acetonitrile-d_3. The transient spectra presented in the figures are a composite of spectra recorded in acetonitrile and acetonitrile-d_3. The signal/noise ratio of spectra recorded in acetonitrile and acetonitrile-d_3 differ and as a result vary within a figure. Kinetic studies were performed at the most prominent IR bands of the ground states of **1** and **2** and of the IR-active transient species produced by LFP. The carriers of transient absorption have a lifetime of 1 ± 0.2 μs (Supporting Information (SI) Figures S1 and S2) in the absence of oxygen, and under these conditions the ground-state vibrational bands of **1** and **2** recover with the same time constant. Oxygen quenches psoralen triplet excited states to produce singlet oxygen or superoxide radical anion, in some cases in high yields.[17] Thus the sensitivity of the transients (produced by LFP of **1** and **2**) to oxygen (SI Figures S1 and S2) encourages us to assign the carriers of the transient spectra to ^{3}**1*** and ^{3}**2***.

The triplet excited states of khellin and visnagin present similar spectral features with moderately intense bands between 1400 and 1600 cm^{-1}. The depletion of the ground-state carbonyl bands is observed between 1600 and 1700 cm^{-1}. DFT calculations allow us to assign the IR bands (Table 1). Our calculations predict that two of the most intense IR bands of **1** will be found at 1645 and 1599 cm^{-1} and those of sensitizer **2** at 1668 and 1601 cm^{-1} are due to their carbonyl C═O and pyrone double bond C═C stretches, respectively. We observed prominent bands of the ground state of **1** in the IR spectra at 1658 and 1625 cm^{-1} (Figure 1) and of the ground state of **2** at 1661 and 1617 cm^{-1} (Figure 3), presumably due to the carbonyl and pyrone C═C stretching vibrations predicted by the DFT calculations. The furan double bond is predicted to have very low IR intensity in ground-state **1** and **2**; however, the furan double bonds in the visnagin and khellin triplet excited states are reported to be the main site of photoreactivity of the furochromones.[18,19]

Upon photoexcitation from ground state to excited state, IR stretching bands are, of course, expected to shift. The triplet excited state of khellin has bands near 1596 and 1525 cm^{-1}, and the triplet excited state of visnagin has a similar IR spectra profile with bands at 1586 and 1521 cm^{-1}. We believe the IR bands at 1525 and 1521 cm^{-1} in Figures 1 and 3 should be assigned to the carbonyl C═O bands of ^{3}**1*** and ^{3}**2***, respectively.

A previous study compared the IR spectra of triplet excited state unlabeled, doubly (carbonyl and pyrone) ^{18}O-labeled, and pyrone ^{18}O-labeled visnagin.[19] It was demonstrated that the 1586 cm^{-1} band was the only signal in the triplet that shifted upon pyrone ^{18}O-labeled substitution; thus the 1586 cm^{-1} band was believed to be the pyrone C═C bond of the triplet state.

DFT calculations do not predict a shift of this vibrational frequency; however, Figures 1 and 3 show that the 1625 and 1617 cm^{-1} pyrone C═C bands for **1** and **2**, respectively, shift to 1596 and 1586 cm^{-1} in their respective triplet states. This is a relatively minor shift, indicating that there is little electron reorganization within this bond upon excitation, and this observation is consistent with the known lack of photoreactivity at this site of the molecule.[18,19] The band of ^{3}**1*** observed at 1405 and 1457 cm^{-1} is attributed to the predicted bands at 1334 and 1413 cm^{-1} of the furan and phenyl double bond C═C stretching bands of ^{3}**1*** (Figure 2). The 1404 and 1449 cm^{-1} bands of ^{3}**2*** are associated with predicted bands at 1381 and 1427 cm^{-1}, respectively (Figure 4). The calculations do not consider Fermi resonance; therefore the intensities of the predicted bands can differ from the experimental spectra. The spectroscopic assignments are in reasonable agreement with DFT calculations.

Radical Anions of Khellin and Visnagin. We examined the transient species formed when **1** and **2** are photoexcited in the presence of strong electron donors, NaI and KSCN, in an attempt to convert triplets **1** and **2** to their corresponding radical anions via electron transfer, as shown in Scheme 1. The predicted spectra of $\mathbf{1}^{\bullet -}$ and $\mathbf{2}^{\bullet -}$ (Figures 6 and 8) are similar to those predicted for ^{3}**1*** and ^{3}**2*** (Figures 2 and 4). The experimental spectra (Figures 5 and 7) recorded in the presence of donor are similar to those of ^{3}**1*** and ^{3}**2***, but the lifetimes of the carriers

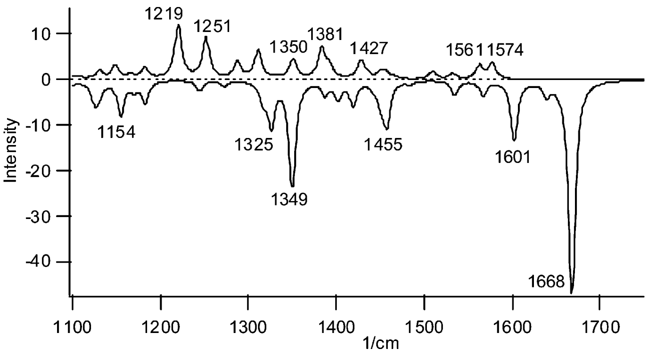
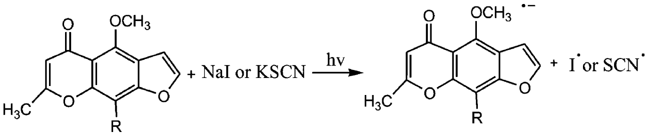


Figure 4. Calculated IR spectra of **2** (down) and ^{3}**2*** (up) in the gas phase.

SCHEME 1: Proposed Mechanism of Reaction of Khellin and Visnagin Triplet States with NaI To Form Their Corresponding Radical Anions



of the transient spectra are much longer in the presence of the electron donor. This indicates that the triplets and radical anions derived from **1** and **2** have prominent IR bands at similar wavelengths, but that the radical anions are the longer lived species. This same tendency was noted previously in a study of flavin triplets and radical anions.[13] The transient spectrum produced upon 266 nm LFP of **2** and 1 mM NaI presents an intense peak at 1594 cm^{-1} (Figure 7) that corresponds to the pyrone C═O stretching IR band, and is in good agreement with the calculated spectrum for **2**$^{\bullet-}$, which predicts a peak at 1607 cm^{-1} for **2**$^{\bullet-}$ (Figure 8). The transient absorption observed in the presence of **2** and 1 mM sodium iodide has a lifetime of greater than 10 μs. Figure 7 demonstrates that other **2**$^{\bullet-}$ bands cannot be assigned due to their strong overlap with IR bands of ^{3}**2***.

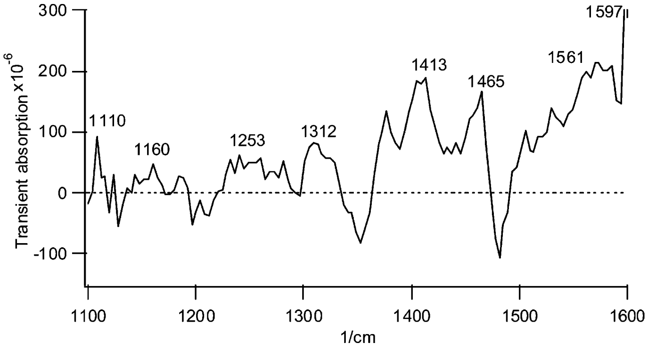


Figure 5. Transient IR spectra produced upon LFP (266 nm) of 6 mM **1** and 10 mM KSCN in argon-saturated acetonitrile (1100−1300 cm^{-1}) and deuterated acetonitrile (1300−1600 cm^{-1}). Window: 0−1 μs. **1** (down); ^{3}**1*** and **1**$^{\bullet-}$ (up).

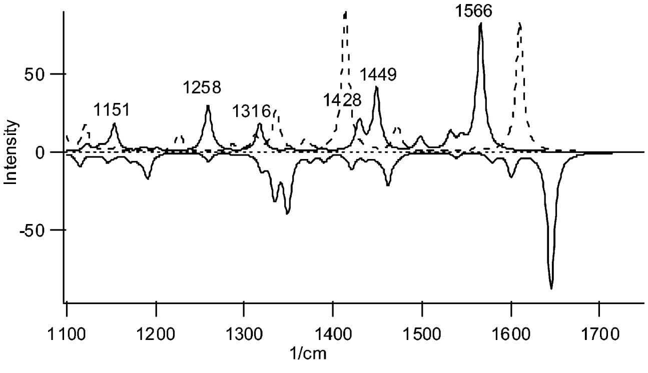


Figure 6. Calculated IR spectra of **1** (down), **1**$^{\bullet 2-}$ (up), and ^{3}**1*** (---) in acetonitrile.

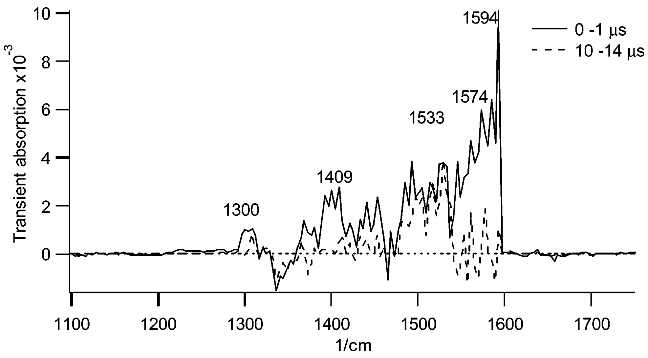


Figure 7. Transient IR spectra produced upon LFP (266 nm) of 10 mM **2** and 1 mM NaI in argon-saturated acetonitrile (1100−1300 and 1600−1750 cm^{-1}) and deuterated acetonitrile (1300−1600 cm^{-1}). The sharp line of demarcation at 1600 cm^{-1} is the boundary between spectra recorded in acetonitrile and acetonitrile-d_3. **2** (down); ^{3}**2*** and **2**$^{\bullet-}$ (up).

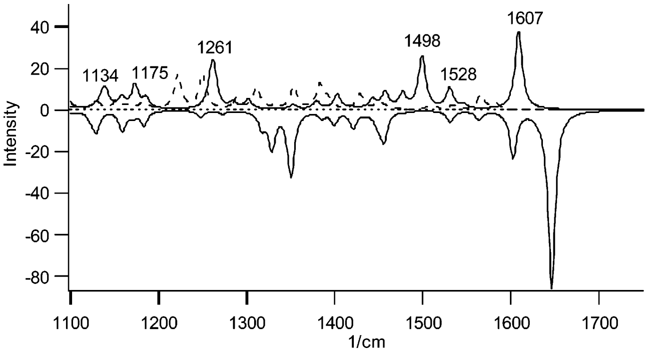


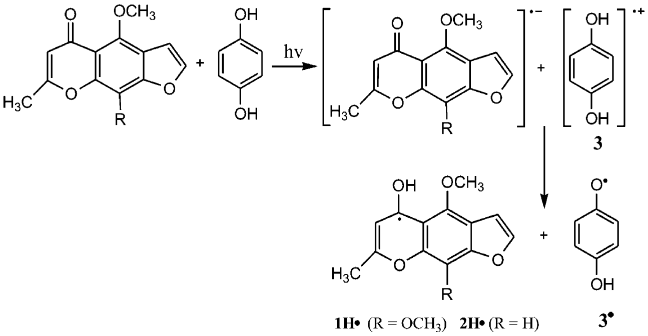
Figure 8. Calculated IR spectra of **2** (down), **2**$^{\bullet 2-}$ (up), and ^{3}**2*** (---) in gas phase.

Similar observations were made on the radical anion of khellin **1**$^{\bullet-}$, which DFT calculations predict will have an intense band at 1566 cm^{-1}, which corresponds to the pyrone C═O stretching IR band (Figure 6). Figure 5 shows that the transient spectrum produced upon 266 nm LFP of **1** in the absence and presence of 10 mM KSCN presents a broad IR band from 1500 to 1600 cm^{-1} where the ^{3}**1*** and **1**$^{\bullet-}$ IR bands overlap; therefore, additional assignments of TRIR bands of **1**$^{\bullet-}$ cannot be achieved.

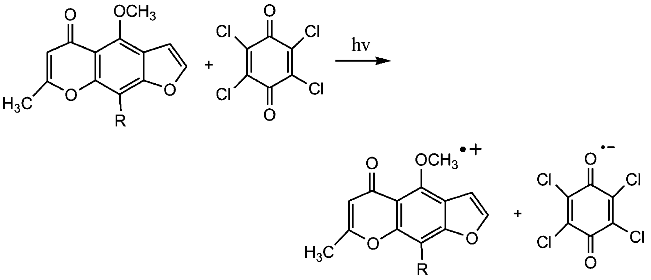
Chloranil Radical Anion and the Radical Cations of Khellin and Visnagin. Wood and Johnston have shown that chloranil can serve as an electron acceptor in photochemical electron-transfer reactions to produce psoralen radical cations as shown in Scheme 3.[8] Thus we studied the transients formed upon LFP of chloranil in the absence and presence of electron-transfer agents. Upon 266 nm LFP of chloranil (Figure 9a) ground-state bleaching is absorbed at 1108, 1569, 1625, and 1693 cm^{-1} (Table 1). New bands are observed at 1156, 1206, 1525, and 1550 cm^{-1} (Figure 9a). These bands are assigned to triplet chloranil because they are quenched in the presence of oxygen and are consistent with the predictions of DFT (Figure 10, Table 1) calculations.

One expects triplet chloranil and iodide ion to react via electron transfer to form chloranil radical anion and iodine atom. LFP (266 nm) of a mixture of 10 mM chloranil and 1 mM NaI produces the TRIR spectrum of Figure 9b. The prominent bands observed at 1144, 1525, 1606, and 1653 cm^{-1} are assigned to the chloranil radical anion (Table 1).

SCHEME 2: Proposed Mechanism of the Triplet States of Visnagin and Khellin with Hydroquinone



SCHEME 3: Proposed Mechanism of Khellin and Visnagin Triplet States with Chloranil To Form the Analogous Radical Cations



Next we studied the LFP of chloranil in the presence of either khellin or visnagin. In this work the absorbances of khellin, visnagin, and chloranil at 266 nm are similar. Thus, much of the exciting laser pulse is absorbed by chloranil and the excited states of khellin, visnagin, and chloranil are all involved in light-induced electron transfer to eventually form the radical cations of **1** and **2** and the chloranil radical anion. The calculated spectra of **1**$^{\bullet+}$ and **2**$^{\bullet+}$ (Figures 12 and 14) are similar, with major IR peaks predicted at 1677, 1574, 1463, 1402, 1342, and 1128 cm^{-1} for **1**$^{\bullet+}$ and at 1662, 1626, 1406, 1346, and 1126 cm^{-1} for **2**$^{\bullet+}$. The active modes are given in Tables 1 and 2. Figures 11 and Figure 13 show the formation of four new peaks at 1136 cm^{-1}, 1425 cm^{-1} (1421 cm^{-1} in the case of **2**), 1530 cm^{-1} (1525 cm^{-1} in the case of **2**), and 1674 cm^{-1} (1658 cm^{-1} in the case of **2**) upon 266 nm photoexcitation of khellin and visnagin in the presence of 10 mM chloranil. However, the only new IR peaks that can be assigned to radical cations **1**$^{\bullet+}$ and **2**$^{\bullet+}$ both are detected at 1136 cm^{-1}, which corresponds to the pyrone C−O stretching IR band of both compounds, as previous experiments demonstrated that the LFP of 10 mM chloranil in acetonitrile

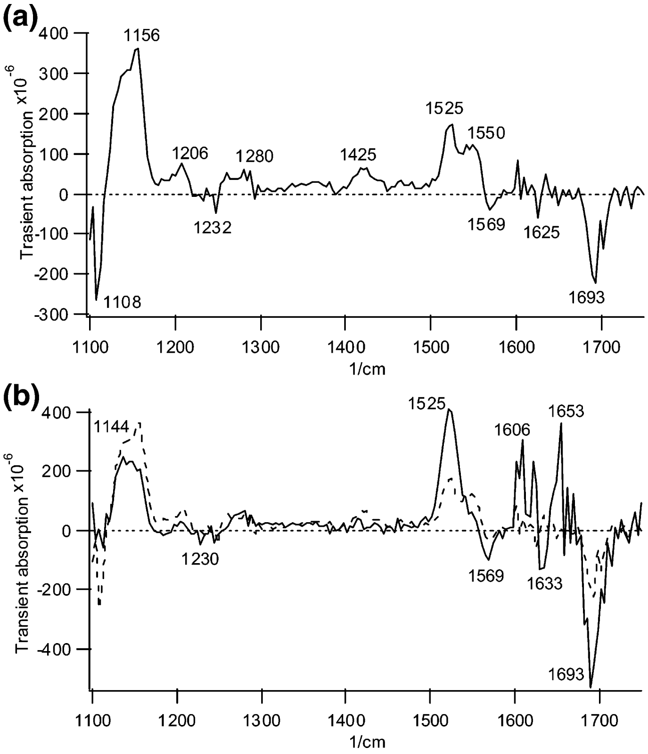


Figure 9. (a) Transient IR spectra produced upon LFP (266 nm) of 10 mM chloranil in argon-saturated acetonitrile (1100−1300 and 1600−1750 cm^{-1}) and deuterated acetonitrile (1300−1600 cm^{-1}). Window: 0−1 μs. S$_o$ (down) and T$_1$ (up). (b) Transient IR spectra produced upon LFP (266 nm) of (—) 10 mM chloranil and 1 mM NaI and (---) 10 mM chloranil in argon-saturated acetonitrile (1100−1300 and 1600−1750 cm^{-1}) and deuterated acetonitrile (1300−1600 cm^{-1}). Window: 0−1 μs. S$_o$ (down); radical anion and T$_1$ (up).

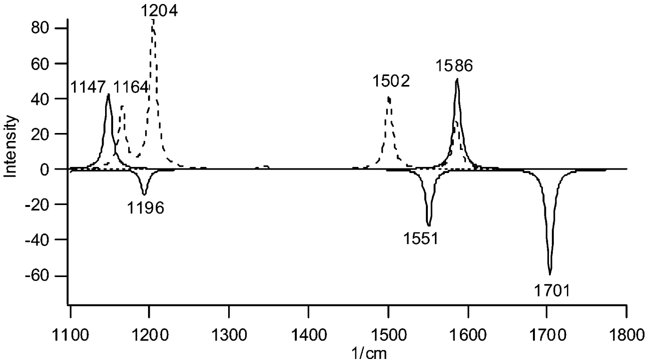


Figure 10. Calculated IR spectra of chloranil (down), chloranil$^{\bullet-}$ (up), and ^{3}chloranil* up (---) in acetonitrile.

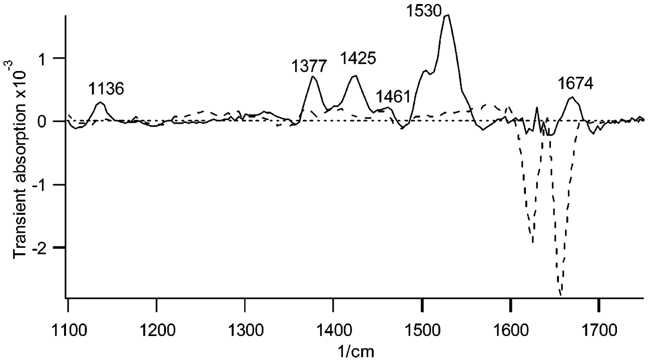


Figure 11. Transient IR spectra produced upon LFP (266 nm) of 6 mM **1** (—) and 10 mM chloranil and 6 mM **1** (---) in argon-saturated acetonitrile (1100−1300 and 1600−1750 cm^{-1}) and deuterated acetonitrile (1300−1600 cm^{-1}). Window: 0−1 μs. **1** and chloranil S$_o$ (down) and ^{3}**1***, **1**$^{\bullet+}$, radical anion, and T$_1$ (up) of chloranil.

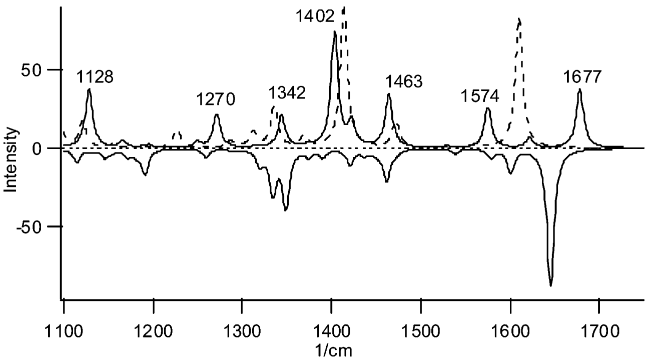


Figure 12. Calculated IR spectra of **1** (down), **1**$^{\bullet+}$ (up), and ^{3}**1*** (---) in acetonitrile.

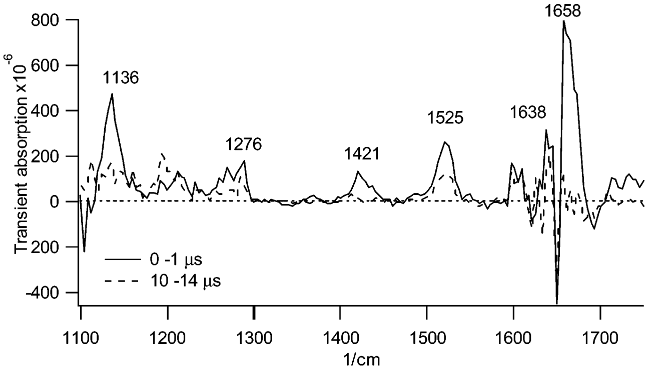


Figure 13. Transient IR spectra produced upon LFP (266 nm) of 10 mM **2** and 10 mM chloranil in argon-saturated acetonitrile (1100−1300 and 1600−1750 cm^{-1}) and deuterated acetonitrile (1300−1600 cm^{-1}). Window: (—) 0−1 μs; (---) 10−14 μs.

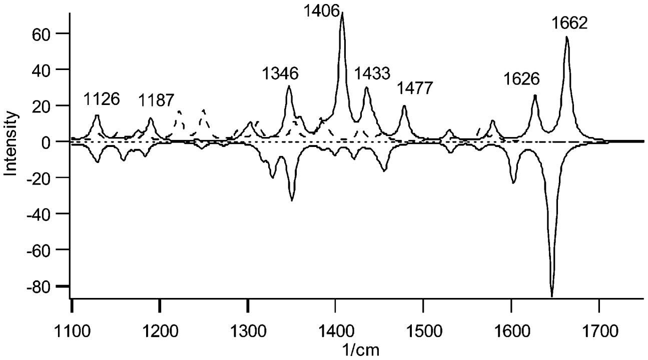


Figure 14. Calculated IR spectra of **2** (down), **2**$^{\bullet+}$ (up), and ^{3}**2*** up (---) in gas phase.

TABLE 2: Experimental and Calculated Frequencies for Visnagin Ground State 2, ^{3}2*, 2$^{\bullet-}$, 2$^{\bullet+}$, and 2H$^{\bullet}$ and Hydroquinone Radical

species	observed bands[a] (cm^{-1})	DFT-predicted bands[b] (cm^{-1})	DFT-predicted rel intensities	mode
2	1661	1668	45.0	C═O stretching
	1617	1601	13.0	pyrone C═C stretching
	1473	1455	10.3	furan C═C stretching
	1341	1349	22.0	C−H bending, C−O stretching
^{3}**2***	1586	1574	3.3	pyrone C═C stretching
	1521	1561	3.0	C═O stretching
	1449	1427	3.5	furan C═C stretching
	1404	1381	7.0	phenyl C═C stretching
	1372	1350	4.7	C−O stretching
	1269	1251	8.8	C−H bending
2$^{\bullet-}$	1594	1607	37.4	C═O stretching
2$^{\bullet+}$	1136	1126	13.5	pyrone C−O stretching
2H$^{\bullet}$		1254	25.5	C−H, O−H bending
	1225	1207	21.8	C−H rocking
		1166	8.1	C−H bending
3H$^{\bullet}$	1597	1579	22.5	C═O stretching
	1537	1485	13.4	O−H bending
	1376	1322	10.4	C−O stretching
	1280	1285	15.7	C−H rocking
	1144	1152	21.6	C−H bending

[a] TRIR. [b] B3LYP calculations with the 6-31G* basis set after scaling by a factor of 0.9613.

and acetonitrile-d_3 upon 266 nm LFP (Figure 9) produces transient peaks at 1150, 1425, and 1525 cm^{-1} (Table 1) of the chloranil triplet excited state and the peak at 1674 cm^{-1} (1658 cm^{-1} in the case of **2**) is due to the chloranil radical anion.

Neutral Radicals Derived from Khellin and Visnagin. Scheme 2 describes an electron transfer followed by a hydrogen atom transfer reaction of hydroquinone with ^{3}**1*** and ^{3}**2***. First, we obtained the authentic spectrum of semiquinone radical **3H**$^{\bullet}$ by LFP of chloranil and hydroquinone (SI Figure S3). In addition to bands attributable to chloranil radical anion, new bands were observed at 1144 and 1280 cm^{-1} assigned to CH bending and rocking modes of semiquinone radical **3H**$^{\bullet}$ based on DFT calculations (Table 1 and SI Figure S4).

The transient spectra produced by LFP of khellin **1** in the presence of hydroquinone does not present the formation of new IR distinct bands for **1H**$^{\bullet}$ (SI, Figure S5) in the region predicted by DFT calculations (SI, Figure S6). In contrast, the TRIR spectra produced upon 266 nm LFP of 10 mM **2** and 10 mM hydroquinone (SI, Figure S7) does contain intense new peaks at 1152, 1225, and 1280 cm^{-1}. The peaks at 1152 and 1280 cm^{-1} are readily attributed to semiquinone radical **3H**$^{\bullet}$ as in the chloranil sensitized reaction. However, the band observed at 1225 cm^{-1} is most likely associated with the predicted (Table 1, Figure S8) C−H rocking mode of **2H**$^{\bullet}$ expected at 1207 cm^{-1}.

IV. Conclusions

With the aid of DFT calculations, the visnagin and khellin triplet excited states were detected by TRIR spectroscopy in acetonitrile. Visnagin and khellin triplet excited states react with chloranil to form their radical cations and the chloranil radical anion. The radical cation of khellin and visnagin each has a vibrational band at 1136 cm^{-1}. The excited states of khellin, visnagin, and chloranil are all involved in the light-induced electron transfer reaction. ^{3}**1*** and ^{3}**2*** both react with anionic electron donors (NaI or KSCN) to form the related radical anions which have vibrational bands at 1561 cm^{-1} for **1**$^{\bullet-}$ and 1594 cm^{-1} for **2**$^{\bullet-}$. Triplet visnagin reacts with hydroquinone to form semiquinone radicals. The vibrational band at 1225 cm^{-1} of the visnagin-derived radical was assigned to C−H rocking mode on the basis of DFT calculations.

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Supporting Information Available: The decay of triplet khellin and visnagin and the kinetics of recovery of their ground-state absorption, TRIR spectra obtained in the presence of hydroquinone, the DFT-calculated IR spectra of transient species, and the Cartesian coordinates of the optimized geometries of triplet states, radical anions, and cations, and neutral radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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