

# Time-Resolved Step-Scan Fourier Transform Infrared Spectroscopy of Triplet Excited Duroquinone in a Zeolite

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Received: July 16, 1996; In Final Form: October 28, 1996<sup>⊗</sup>

The infrared spectrum of triplet excited duroquinone occluded in zeolite NaY has been recorded by time-resolved Fourier transform-infrared spectroscopy on the nano- and microsecond time scale. A commercial step-scan instrument whose capability was expanded to allow absorption spectroscopy at nanosecond resolution was employed for this study. <sup>18</sup>O isotope labeling allowed assignment of a strong absorption at 1542 cm<sup>-1</sup> to the CO stretching mode. The 100 cm<sup>-1</sup> red shift of this band relative to the CO stretch of the ground state establishes the  $\pi\pi^*$  character of the lowest triplet state of duroquinone. This is consistent with the highly polar environment of the zeolite NaY cage. The lifetime of the excited triplet state is 20  $\mu$ s (–50 °C). This constitutes the first time-resolved infrared spectrum of a transient molecule in a zeolite.

## I. Introduction

Time-resolved vibrational spectroscopy is a powerful approach for elucidating reaction mechanisms because it furnishes information on the structure of chemical intermediates. Our goal is to employ one of its variants for the study of transients in zeolite matrices. Nanopore matrices such as zeolites offer a unique environment for carrying out photoreactions due to their geometrical constraints, polarity, and, therefore, their ability to control the reaction pathways.<sup>1–5</sup> Important requirements for chemical systems of interest to us are access to the entire mid-infrared range (4000–400 cm<sup>-1</sup>) and the time domain from nanoseconds to milliseconds. Of the two main techniques available, time-resolved infrared and resonance Raman spectroscopy, the latter has been used in zeolites by the groups of Kincaid and Dutta for dynamic studies on transition metal complexes.<sup>6,7</sup> However, this method is not suitable for small molecule chemistry because reactants and transients typically lack the chromophores required for resonance enhancement. By contrast, the routine use of static infrared spectroscopy as a tool for monitoring chemical processes in zeolites suggests that time-resolved IR would be suitable for elucidation of elementary reaction steps in these matrices. Yet, with the exception of a vibrational relaxation study of surface OH groups,<sup>8</sup> there have been no reports thus far on time-resolved infrared spectroscopy in zeolites or other molecular sieves.

An ideal method for broad-band infrared monitoring of condensed phase processes in the nano- and microsecond regime is step-scan Fourier transform infrared (FT-IR) absorption spectroscopy. The best time resolution that has been reached to date with this method is around 500 ns.<sup>9,10</sup> Higher resolution (50 ns) has been reported for step-scan emission measurements.<sup>11</sup> However, the signal processing method used in step-scan emission spectroscopy is not suitable for sensitive transient absorption measurements for reasons presented in section II. Alternative infrared methods for monitoring condensed phase reactions are based either on dispersive IR spectrometers or on CW laser sources. Dispersive IR spectrometers have been extensively used in transient spectroscopy of transition metal complexes for monitoring of CO and CN ligands<sup>12,13</sup> and for recording of nano- and microsecond processes of organic and

biological molecules.<sup>14</sup> The dispersive infrared method lacks the multiplex and throughput advantages of the FT-IR method and is therefore much less efficient. This becomes especially a problem for spectroscopy in the fingerprint region where bending and skeletal stretching modes often have small absorption cross sections. For laser spectroscopy, tunable infrared emitting semiconductor diodes and fixed frequency CO lasers have been used. The high intensity of these monochromatic sources allows recording even in the low nanosecond regime.<sup>13,15–18</sup> Unfortunately, the laser methods do not allow spectroscopy over more than a few hundred cm<sup>-1</sup> typically because of limited tuning ranges. By contrast, the step-scan infrared method gives access to the entire infrared region. The time resolution is only limited by the duration of the photolysis laser pulse, the response time of the infrared detector, and the bandwidth of the data acquisition electronics.

Access to the nanosecond time regime and the full infrared region is crucial for capturing chemical intermediates in ambient temperature matrices. For this reason, we have expanded the resolution of step-scan FT-IR absorption spectroscopy to 20 ns and demonstrated such spectra in a recent study of the bacteriorhodopsin photocycle.<sup>19</sup>

As a first system, we have chosen a triplet excited benzoquinone occluded in cation-exchanged zeolite Y. Aromatic carbonyl compounds in general, and quinones in particular, have two low-lying triplet states with  $n\pi^*$  and  $\pi\pi^*$  character, respectively.<sup>20</sup> In the case of the  $n\pi^*$  state, a nonbonding electron of the carbonyl oxygen is promoted to an antibonding  $\pi^*$  orbital, while a  $\pi$  electron is excited to the  $\pi^*$  orbital in the case of the  $\pi\pi^*$  state. The energetics of these two states is influenced by the polarity of the solvent. This is due to the fact that the  $\pi\pi^*$  state has a larger dipole moment than the  $n\pi^*$  state.<sup>20</sup> In fact, the relative ordering of the two states may depend on the solvent. The importance of this is that  $n\pi^*$  states of carbonyls are more reactive than the  $\pi\pi^*$  states. Hence, the chemical behavior of the lowest triplet state depends on whether it has  $n\pi^*$  or  $\pi\pi^*$  character. Vibrational spectroscopy is a reliable diagnostic tool for determining the nature of the triplet state; in the case of a  $\pi\pi^*$  state, the CO group retains in essence its double bond, and the red shift of the mode relative to ground state is only about 100 cm<sup>-1</sup> as has been shown for 4-phenylbenzophenone by dispersive infrared<sup>21</sup> and resonance Raman

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1996.

spectroscopy.<sup>22</sup> By contrast, the CO group of  $n\pi^*$  triplet states has single bond character and lies, therefore, at much lower frequencies (1200–1300  $\text{cm}^{-1}$ ). This has been observed in the case of the triplet  $n\pi^*$  state of benzophenone by time-resolved resonance Raman<sup>23</sup> and phosphorescence excitation spectroscopy.<sup>24</sup>

In this paper, we report the infrared spectrum of triplet excited duroquinone in zeolite NaY on the nano- and microsecond time scale. This is the first time-resolved infrared spectrum of a transient molecule in a zeolite and the first IR spectrum of a triplet quinone in any medium. In addition, a detailed description of the sensitive step-scan FT-IR absorption spectrometer used in this work is presented.

## II. Experimental Section

**Step-Scan FT-IR Instrument.** The time-resolved step-scan instrument consists of a Bruker Model IFS88 spectrometer, a 486 PC with Bruker OPUS software, and auxiliary electronics for matching nanosecond infrared signals to a 200 MHz 8 bit digitizer (Model PAD 82 supplied by Bruker).

A key requirement for transient absorption measurements at high sensitivity is recording of the ac-coupled detector output. Previous workers have used dc signals only,<sup>11,25,26</sup> with the exception of Siebert.<sup>9</sup> By contrast to infrared emission measurements,<sup>11</sup> use of the dc interferogram for time-resolved absorption measurements severely limits the achievable signal-to-noise performance because the static interferogram is orders of magnitude larger than the laser-induced signal of interest. The limitation is particularly serious in the case of nanosecond measurements with an 8 bit digitizer. Siebert was the first to implement ac-coupled step-scan spectroscopy in an instrument with microsecond time resolution.<sup>9c</sup> Here, only the laser-induced change of the interferogram signal is recorded. For the measurements reported here, we have equipped our spectrometer with a photovoltaic HgCdTe detector featuring simultaneous ac and dc outputs (Kolmar Technologies Model KMPV11-1-J2, 50 ns resolution). The resolution refers to the fwhm of the detector response to a 1.064  $\mu\text{m}$  Nd:YAG pulse of 9 ns fwhm. The RC decay constant of the ac coupler is 3.0 ms. Separate system configurations were used for nanosecond and microsecond experiments, which will be described in turn.

Nanosecond measurements were conducted with the 200 MHz digitizer and simultaneous recording and processing of the ac- and dc-coupled interferometric signals. Corresponding software and hardware capabilities were implemented in collaboration with Bruker engineers. Sampling intervals were 10 ns. Fourier transformation of the ac-coupled interferogram time slices uses the phase obtained from the dc-coupled interferogram. In order to assure use of the full dynamic range of the 8 bit digitizer ( $\pm 1$  V full range), the ac-coupled signal was amplified by a factor of 100 (CAL-AV Laboratories Model 7930 500 MHz amplifier) before transfer to the digitizer. The dc output of the detector was first adjusted to ground and then amplified (LeCroy Model 6103 programmable 150 MHz and CAL-AV amplifiers) in order to reach close to  $\pm 1$  V peak-to-peak interferogram amplitude before entering the digitizer.

Measurements on the microsecond time scale were done with a 200 kHz digitizer. Since no simultaneous processing capability for ac- and dc-coupled signals is available for this digitizer, a dc-coupled step-scan run of the sample was conducted first in order to determine the phase (no excitation of the sample). The phase was stored and then used for the Fourier transformation of the ac-coupled interferogram time slices measured subsequently.

Of crucial importance for measurement at high sensitivity is a high stability of the stepping mirror by minimizing acoustic

and mechanical noise in the laboratory. By use of a vibration decoupled table Newport Model RS4000, a mirror stability of  $\pm 1.4$  nm was achieved. The latter was calculated from the peak-to-peak noise of the signal of the HeNe laser when the mirror was held in a fixed position.

**Laser Excitation Source.** For excitation of the sample at 355 nm, the third harmonic of a Quanta-Ray Nd:YAG laser Model DCR-2A (with GCR-3 optics) was used. The repetition rate was 10 Hz, and we used 4 mJ pulse<sup>-1</sup> typically (80  $\mu\text{J}$   $\text{mm}^{-2}$ ). A small prism (1 cm edge to edge) was used to align the UV photolysis beam (1 cm diameter) collinear with the infrared probe beam. A germanium plate of 1.5 mm thickness prevented photolysis light from hitting interferometer mirrors and the IR detector element. In addition, a dielectrically coated filter (OCLI No. W07100-11X) was mounted in front of the infrared detector in order to limit the bandwidth to the region between 2250 and 1130  $\text{cm}^{-1}$  (= natural folding limits; the zeolite matrix absorbs strongly below 1200  $\text{cm}^{-1}$ ). For triggering of the digitizer, a small fraction of the 355 nm pulse was exposed to an EG+G silicon photodiode Model SGD-444. The Nd:YAG laser was kept in a separate room in order to prevent any rf emission from interfering with the infrared detector electronics.

**Sample Preparation.** Zeolite NaY (LZ-Y52, Aldrich Chemical Co., Lot No. 03319TX) was pressed into self-supporting wafers of 12 mm diameter and had 5–10 mg weight. The pellets were mounted inside a home-built miniature infrared cell described previously.<sup>27</sup> The infrared cell was mounted inside a variable temperature Oxford cryostat Model DN1714 (77 K to 200 °C).<sup>27</sup> Prior to loading of duroquinone from the gas phase, the zeolite pellet was dehydrated at 200 °C in the high-vacuum cell for 10 h. Duroquinone (tetramethyl-1,4-benzoquinone, Aldrich, 97%) was recrystallized three times from ethanol before loading. All experiments were conducted at  $-50$  °C in order to minimize thermal effects (see section III).

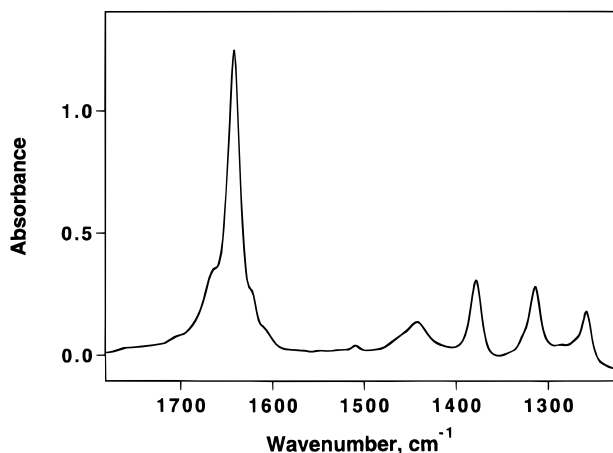
<sup>18</sup>O-labeled duroquinone was prepared according to a literature procedure.<sup>28</sup> A 0.075 g sample of duroquinone was dissolved in a solution containing 0.27 mL of  $\text{H}_2^{18}\text{O}$  (Cambridge Isotope Laboratories, 97%), 0.18 mL of trifluoroacetic acid (Aldrich, 99%), and 1.05 mL of tetrahydrofuran (Aldrich, 99.9%). The solution was purged with nitrogen in a 3 mL glass tube and sealed with a Teflon stopper and paraffin film. After keeping the solution at 40 °C for 7 days, the solvent was evaporated under vacuum, and the <sup>18</sup>O-exchanged duroquinone was purified by repeated vacuum distillation. Mass spectrometric analysis (electron impact) indicated that the final product contained 52% of the duroquinone with <sup>18</sup>O on both carbonyls, 40% with <sup>18</sup>O on only one of the carbonyls, and 8% unlabeled duroquinone. This result is very similar to a previous report in the literature.<sup>28</sup>

## III. Results and Discussion

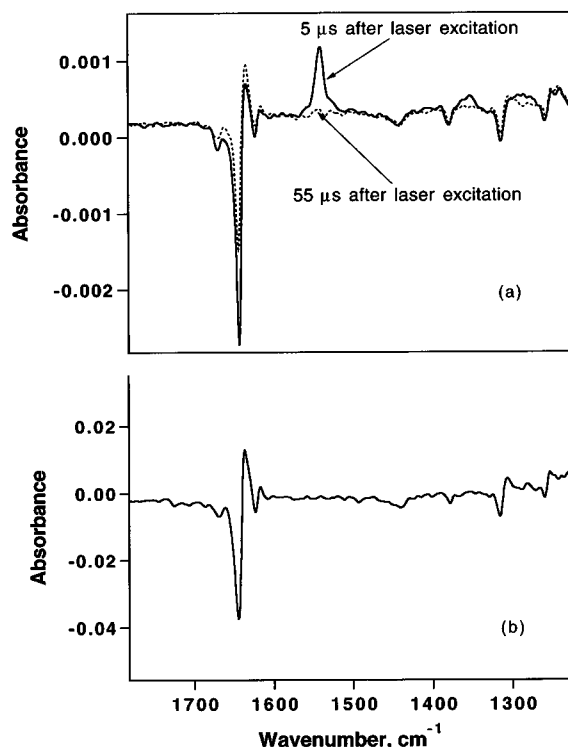
A static infrared spectrum of duroquinone occluded in zeolite NaY at  $-50$  °C is shown in Figure 1. Step-scan experiments were conducted at a spectral resolution of 4  $\text{cm}^{-1}$ . With the folding limits at 2250 and 1130  $\text{cm}^{-1}$ , this resulted in 570 mirror positions per step-scan experiment. At each mirror position, 25 laser-induced decays were averaged, resulting in 30 min measurement time per experiment. Two spectral time slices are shown in Figure 2a: one taken 5  $\mu\text{s}$  after the laser pulse and the other 55  $\mu\text{s}$  after the pulse. These absorbance difference spectra were computed as

$$\Delta A = -\log\left(\frac{S + \Delta S}{S}\right)$$

where  $S$  stands for static single beam spectrum (Fourier



**Figure 1.** FT-IR difference spectrum before and after vacuum loading of duroquinone into zeolite NaY.

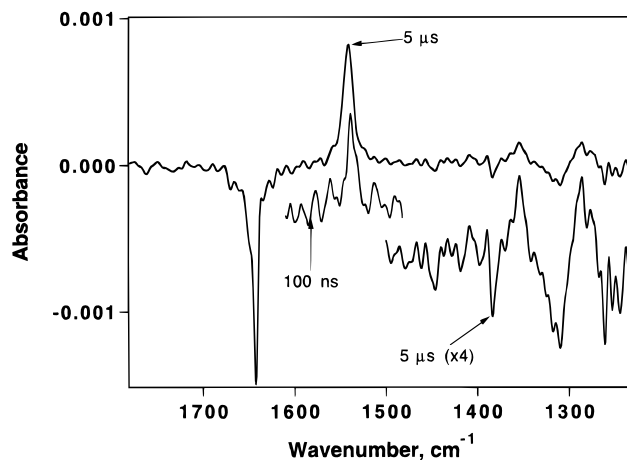


**Figure 2.** (a) Transient FT-IR spectra recorded 5 and 55  $\mu$ s after laser excitation of duroquinone in NaY at  $-50$   $^{\circ}$ C (84 experiments were averaged). (b) FT-IR difference spectrum of duroquinone in NaY before and after temperature increase from  $-50$  to  $-30$   $^{\circ}$ C.

transform of the dc-coupled interferogram) and  $\Delta S$  the laser-induced spectrum (Fourier transform of the ac-coupled interferogram normalized for amplification).<sup>9c</sup>

A glance at the two spectral time slices reveals two distinct types of kinetic behavior: (i) positive bands such as those at 1542, 1354, and 1286  $\text{cm}^{-1}$  that completely vanish within 50  $\mu$ s; (ii) negative features at 1642, 1442, 1380, 1313, and 1259  $\text{cm}^{-1}$  which decrease only partially over the first 50  $\mu$ s. These latter bands overlap with those of ground state duroquinone, but the peaks are displaced by a few  $\text{cm}^{-1}$ . In addition, some of these features (1640, 1310, 1260  $\text{cm}^{-1}$ ) exhibit dispersive shapes. This phenomenon is characteristic for a small transient temperature change induced by the laser pulse and is well described in the literature.<sup>14a</sup>

When repeating the same step-scan experiment with a duroquinone-loaded zeolite, but this time by exposing the pellet to 1 atm of  $\text{O}_2$  gas, only bands coinciding with type ii features

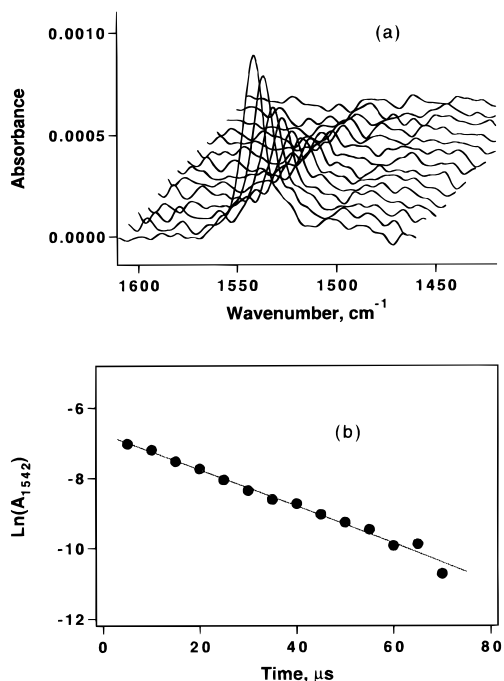


**Figure 3.** Transient FT-IR spectrum of triplet duroquinone at 5  $\mu$ s after the laser pulse. It was obtained by subtracting the 55  $\mu$ s spectrum from the 5  $\mu$ s spectrum shown in Figure 2a (see text). An insert shows the spectrum below 1500  $\text{cm}^{-1}$  expanded by a factor of 4. Another insert shows the  $\nu(\text{CO})$  band recorded during the first 100 ns after the laser flash (16 experiments were averaged). All experiments were conducted with the fwhm = 50 ns resolution MCT detector.

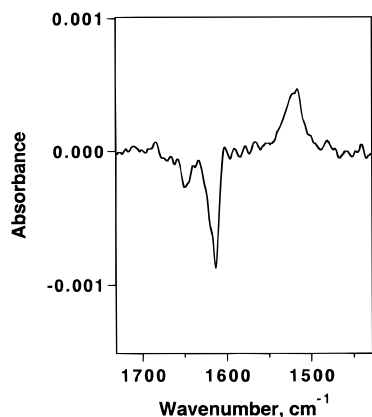
of Figure 2a were observed. No absorptions of set i appeared. This strongly supports our explanation of type ii features in terms of a transient thermal effect induced by the UV laser pulse. In fact, a spectrum resembling the 55  $\mu$ s trace of Figure 2a was obtained when recording the infrared difference spectrum before and after a temperature rise of the NaY matrix. This is shown in Figure 2b. Note that the increase of the bulk zeolite temperature by 20 deg gives an approximately 20 times larger signal than in Figure 2a. This implies that the laser heating effect is a few degrees at the most.

More importantly, the reversible, quantitative quenching of type i bands upon exposure of the zeolite matrix to  $\text{O}_2$  gas indicates that these originate from triplet duroquinone. At  $-50$   $^{\circ}$ C, 1 atm of  $\text{O}_2$  gas results in about two  $\text{O}_2$  molecules per supercage on average. Hopping of a small diatomic like  $\text{O}_2$  between cages takes only nanoseconds even at this low temperature.<sup>29</sup> Hence, deactivation of triplet excited duroquinone is certainly complete on the nanosecond time scale,<sup>30</sup> consistent with what we observe. Since the decay of the heat-induced bands is at least several milliseconds while the triplet absorptions decay within 50  $\mu$ s, we can obtain the transient infrared spectrum of the  $T_1 \leftarrow S_0$  interconversion by subtracting the 55  $\mu$ s time slice from any preceding time slice. The result for the 5  $\mu$ s spectrum is shown in Figure 3. An insert shows the spectrum in the region 1500–1200  $\text{cm}^{-1}$  on an expanded absorbance scale. Transient product bands are readily observed at 1542, 1354, and 1286  $\text{cm}^{-1}$ . Additionally, two bands were noted at 1408 and 1389  $\text{cm}^{-1}$  with signal-to-noise barely above one, but strictly reproducible. Nanosecond spectra revealed a detector response limited rise of the transient spectrum. A 100 ns time slice of the strongest absorption at 1542  $\text{cm}^{-1}$  is shown in Figure 3. The decay of this band is exponential, with a time constant of  $19.6 \pm 1.0$   $\mu$ s (Figure 4). It is comparable with the lifetime of triplet duroquinone reported in various solvents.<sup>31,32</sup>

$^{18}\text{O}$  substitution of duroquinone results in a 25  $\text{cm}^{-1}$  red shift of the 1542  $\text{cm}^{-1}$  triplet state absorption. None of the other bands of the transient are affected significantly. This shift is close to the 29  $\text{cm}^{-1}$  red shift of the ground state duroquinone C=O stretch at 1642  $\text{cm}^{-1}$ <sup>28</sup> and is typical for a carbon–oxygen bond. However, as illustrated by the 5  $\mu$ s time slice obtained upon excitation of the duroquinone- $^{18}\text{O}$  sample (Figure 5), the shapes of the  $\nu(\text{CO})$  absorption of ground and triplet excited state are very different. The negative band at 1642  $\text{cm}^{-1}$



**Figure 4.** (a) Decay of the transient C=O stretch absorption of triplet duroquinone at 1542  $\text{cm}^{-1}$ . (b) Fit of the absorbance decay yields a single exponential decay time of 19.6  $\mu\text{s}$ .



**Figure 5.** Transient FT-IR spectrum at 5  $\mu\text{s}$  after excitation of the  $^{18}\text{O}$ -labeled duroquinone sample in NaY at  $-50\text{ }^{\circ}\text{C}$ . It was obtained by subtracting the 55  $\mu\text{s}$  spectrum from the 5  $\mu\text{s}$  spectrum (see text). The reproducibility of these band shapes was confirmed in three separate experiments.

originates from the  $\nu(\text{C}^{16}\text{O})$  mode of duroquinone- $^{16}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{18}\text{O}$ , and the depletion at 1613  $\text{cm}^{-1}$  originates from  $\nu(\text{C}^{18}\text{O})$  of the  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}^{18}\text{O}$  species.<sup>28</sup> By contrast, no distinct bands can be discerned from the  $\nu(\text{CO})$  profile of the excited species. There is no such separation into decoupled  $\text{C}^{16}\text{O}$  and  $\text{C}^{18}\text{O}$  stretching modes. All we observe is a shoulder at 1542  $\text{cm}^{-1}$  originating from the unlabeled molecule, followed by a continuous absorbance increase toward 1517  $\text{cm}^{-1}$ , the frequency of the excited  $^{18}\text{O}^{18}\text{O}$  species. We interpret this observation in terms of distinct  $\nu(\text{CO})$  absorptions of the  $^{16}\text{O}^{18}\text{O}$  transient; the  $\nu(\text{C}^{16}\text{O})$  mode absorbs to the red of 1542  $\text{cm}^{-1}$  and  $\nu(\text{C}^{18}\text{O})$  to the blue of 1517  $\text{cm}^{-1}$ . This indicates substantial coupling of the CO stretching modes in the  $\text{T}_1$  state, which contrasts with the lack of coupling in the ground state.<sup>28</sup> It is an interesting manifestation of the different electronic structure of the two states. In the only previous report of vibrational absorptions of triplet duroquinone, a time-resolved resonance Raman study in solution, a band at 1533  $\text{cm}^{-1}$  (acetonitrile) or 1542  $\text{cm}^{-1}$  (ethanol) was assigned to  $\nu(\text{C}=\text{C})$ .<sup>33</sup> No absorption

was assigned to the  $\text{C}=\text{O}$  stretching mode. It is possible that  $\nu(\text{C}=\text{C})$  is too weak for detection by infrared; alternatively, the Raman assignment may have to be reconsidered since no support for the  $\text{C}=\text{C}$  stretch assignment by isotopic labeling was given.<sup>33</sup>

The triplet state absorptions at 1354 and 1286  $\text{cm}^{-1}$  are expected to be predominantly ring CC stretching modes by analogy with the infrared spectrum ground state duroquinone and of benzoquinone.<sup>34,35</sup> The derivative feature around 1385  $\text{cm}^{-1}$  signals a small ( $<10\text{ cm}^{-1}$ ) blue shift of the triplet state mode relative to the ground state fundamental. It is assigned to the symmetric  $\text{CH}_3$  bending mode which is indeed expected to be little affected by the electronic excitation. The small but reproducible triplet absorption at 1408  $\text{cm}^{-1}$  is most likely a mixture of  $\nu(\text{CC})$  and asymmetric  $\text{CH}_3$  bending modes.<sup>34,36</sup>

From the modest red shift of 100  $\text{cm}^{-1}$  for the  $\nu(\text{CO})$  mode, we conclude that the CO group of triplet duroquinone has a double bond. Hence, the lowest triplet state of the molecule has predominantly  $\pi\pi^*$  character. This is consistent with the proposal by Kemp and Porter that the  $\text{T}_1$  state of duroquinone is  $\pi\pi^*$  in polar solvents such as ethanol or water.<sup>32</sup> Zeolite NaY consists of a three-dimensional network of spherical cages (13 Å diameter) interconnected by 7 Å windows. The wall of each cage carries a negative charge of 7, which is counterbalanced by  $\text{Na}^+$  ions, some of them located inside these large cages.<sup>37</sup> It is to be expected that in these highly polar cages the duroquinone molecules will have the polar  $\pi\pi^*$  state as the most stable triplet state, as observed. Strong stabilization of  $\pi\pi^*$  triplet states in cation-exchanged zeolites has been proposed recently for a number of related aromatic ketones.<sup>38</sup>

#### IV. Conclusions

We have recorded the transient infrared spectrum of triplet excited duroquinone isolated in a NaY matrix. The frequency shift of the CO stretching mode of the transient reveals the  $\pi\pi^*$  nature of the lowest triplet state of the quinone. This is consistent with the highly polar environment of the cages inside an alkali zeolite. The lifetime of 20  $\mu\text{s}$  is close to that reported in polar solvents.

These measurements demonstrate the feasibility of broad-band infrared absorption spectroscopy in zeolites on the nano-to millisecond time scale in the 4000–1200  $\text{cm}^{-1}$  region using the step-scan FT method. (Zeolites absorb strongly in most regions below 1200  $\text{cm}^{-1}$ .) It opens up detailed mechanistic studies of any chemical reaction or physical process that can be triggered with a nanosecond laser flash. For example, time-resolved studies of recently established reactions of hydrocarbons with  $\text{O}_2$  under visible light in cation-exchanged zeolite Y can be studied by this method.<sup>5</sup> Such work is in progress.

**Acknowledgment.** This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC03-76SF00098. The authors thank Ms. Elisabeth Gomez, visiting student from N.F.I. Optronique, Universite Paris-Sud, Orsay, for her contribution to the development of instrumentation for the nanosecond step-scan FT-IR measurements.

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