

FREE-JET SPECTRA AND STRUCTURE OF *o*-, *m*- AND *p*-DIHYDROXYBENZENES

T.M. DUNN, R. TEMBREULL and D.M. LUBMAN

The Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA

Received 14 May 1985; in final form 8 July 1985

Analysis of the free-jet spectra of hydroquinone (para), catechol (ortho) and resorcinol (meta) shows the presence of multiple origins in each molecular spectrum which are interpreted as belonging to separate structural isomers.

1. Introduction

The spectra of hydroquinone, catechol and resorcinol were first analyzed under conditions of medium resolution by Beck [1]. At that time (1950) the spectrum was interpreted very much in the same mold as that of other substituted benzenes (particularly the halogenated) in that a single origin was assigned for the electronic transitions in the near ultraviolet ($\approx 35000\text{--}36000\text{ cm}^{-1}$) and the bands at longer wavelengths were attributed to transitions from vibrational levels populated at room temperature (sequences and progressions) while those to shorter wavelengths were assigned to excited state progressions (together with sequences).

The resolution obtainable in this work was relatively modest (perhaps of the order of 50000) and even then the relatively low vapor pressures of these molecules meant that the absorption cell needed to be heated in order to obtain sufficient vapor for a reasonable spectrum (up to 140°C). This high temperature, however, led to considerable diffuseness as a consequence of populating a much greater variety of rotational and vibrational states, the former particularly, leading to the loss of sharp structures in the individual vibronic bands.

The study was extensive and, with one exception, the transitions assigned were convincing. The exception concerns the bands at 33533 and 33499 cm^{-1} in the hydroquinone spectrum which were assigned as the origin and its low-frequency sequence or hot band, 35 cm^{-1} to lower energies. Even the original assign-

ments show that the lower-frequency band is extremely strong but, in the text, it is both identified as a sequence (totally symmetric) and is also said to have a different rotational contour — two heads rather than the single head of the origin. Similar situations with respect to the origin and nearby bands in resorcinol and catechol also appear anomalous and it is now clear that some of these bands previously assigned as sequences are, in reality, the origins of structural isomers of these compounds.

2. Experimental

Two parallel kinds of experiments were performed. The first set of experiments utilizes laser resonant two-photon ionization (R2PI) spectroscopy in supersonic expansions to study the ultracold spectroscopy of these molecules. The supersonic beam time-of-flight mass spectrometer unit used in these experiments is similar to that of our previous work [2]. This device consists of a TOFMS in which a supersonic molecular beam crosses the ion acceleration region where ionization is produced by laser radiation. The laser beam, molecular beam, and time-of-flight ion path are orthogonal to one another. The vacuum system consists of a stainless steel chamber pumped by a 6" diffusion pump with a liquid-nitrogen-cooled baffle to obtain a background pressure of $\approx 10^{-6}$ Torr. The supersonic molecular beam source is produced by using the Quanta-Ray PSV-1 pulsed valve which provides gas pulses of $\approx 55\text{ }\mu\text{s}$ fwhm at "choked flow".

A back pressure of 1 atm Ar, with an orifice diameter of 0.05 cm produced a $M_T \approx 40$. The nozzle to excitation region distance was fixed at 9.25 cm which places the molecular beam well within its "free flow" region [3]. When a pulse rate of 10 Hz was used, the average chamber pressure was 1.5×10^{-5} Torr. The compounds were heated to ≈ 70 – 85°C and a slow continuous flow of Ar gas was swept over the same and into the orifice region in order to ensure a steady concentration of ≈ 30 ppm in the carrier gas. In order to prevent sample from adhering to the walls the valve was heated to between 80 and 100°C during operation.

The ions produced by laser photoionization were detected by using a TOFMS modified for use with a supersonic beam [4]. The detector was a dual microchannel plate (R.M. Jordan Co.) which can provide subnanosecond risetimes needed to process the ultrafast (< 10 ns) pulses provided by the TOF device. The molecular ion was monitored as a function of wavelength using a SRS model 250 gated integrator. Thus, we obtain mass selected ionization spectra of molecules. Any background contaminants or impurities can be gated out by this method. Before passing the laser beam through the ionization region of the TOF device the laser beam was collimated to ≈ 2 mm by using a positive negative (30/10 focal length ratio) lens telescope system. The light beam was then attenuated so that the energy was typically 0.1–0.2 mJ so that *no fragmentation* was obtained under the conditions of these experiments.

The laser source is a Quanta-Ray DCR-1A Nd:YAG laser used at its second harmonic (532 nm) to pump various dyes in the PDL-1A dye laser. For tunable UV light, the output from the dye laser was frequency-doubled in phase-matched KD*P in the WEX-1 wavelength extension device. The dye laser was scanned by using a stepping motor controlled by the CDM-1 control display module.

The second set of experiments involved the high-resolution absorption spectra of these compounds being rephotographed under very much higher resolution (of the order of 500000) using methods and equipment previously described [5]. The spectra were taken in a 1 m fused silica cell uniformly heated and maintained at temperatures up to 150°C . The spectra were recorded photographically and the photographic plates were analyzed using a Joyce-Loebl mark III

microdensitometer. The wavenumbers of bands given here have been vacuum corrected. For the most part, these values are ≈ 3 cm^{-1} lower than the values given by Beck [1] but whether this difference is significant or not must await the calculation of the contours at low (≈ 10 K) temperatures. Finally, there are difficulties in obtaining precise values of the laser wavelengths and, for this region, the errors must be assessed as $\approx \pm 3$ cm^{-1} at this time.

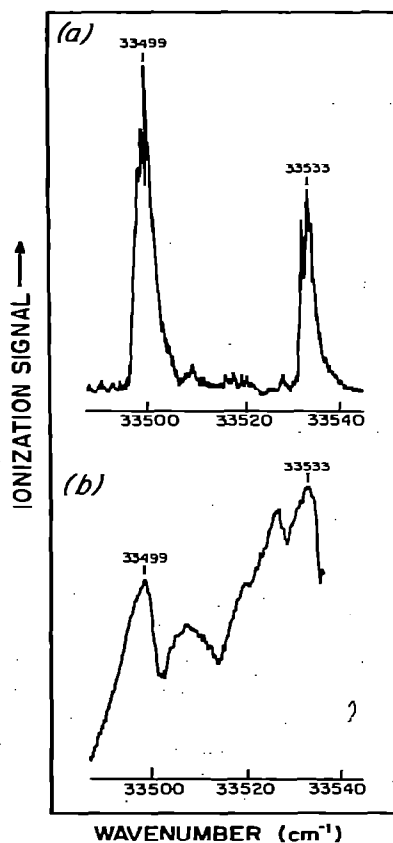


Fig. 1 (a) Resonant two-photon ionization (R2PI) spectrum of hydroquinone expanded in a supersonic jet of 1 atm back pressure of Ar. Gating the signal ensures that only the parent molecular ion is monitored in this spectrum using a TOF mass spectrometer. (b) High-resolution absorption spectrum of hydroquinone.

3. Results

The free jet spectra indicate the presence of two origin bands for hydroquinone at 33533 and 33499 cm^{-1} and three for each of resorcinol and catechol. The hydroquinone spectra in the origin regions are given in fig. 1 and, at the temperature of the jet, the band assigned as hot by Beck cannot be vibrationally populated so that it must arise from the lowest vibrational state of the ground electronic state. The accompanying high-resolution spectrum of hydroquinone shows that the band assigned as a hot band by Beck is at least as intense as the origin and cannot be a sequence. Further, despite some rotational overlapping by a band a few cm^{-1} to higher frequencies (which is a hot band), it is clear that the rotational contour of this band is essentially the same as the

origin. Thus, the free jet spectrum and the high resolution spectrum disclose the presence of *two* origin bands separated by 35 cm^{-1} . The free jet spectrum of catechol and resorcinol gives strong (temperature independent) bands at 35646, 35760 and 35896 cm^{-1} (catechol) and 35943, 36166 and 36192 cm^{-1} (resorcinol) of which at best two in each case, and possibly all three (see below), are assignable as origins.

4. Discussion

We assign the two origin bands of hydroquinone to the *cis* and *trans* isomers and note that their relative intensities are $\approx 2 : 1$ in the free jet spectrum. This suggests that at the temperature at which the hydroquinone was injected into the jet, the popula-

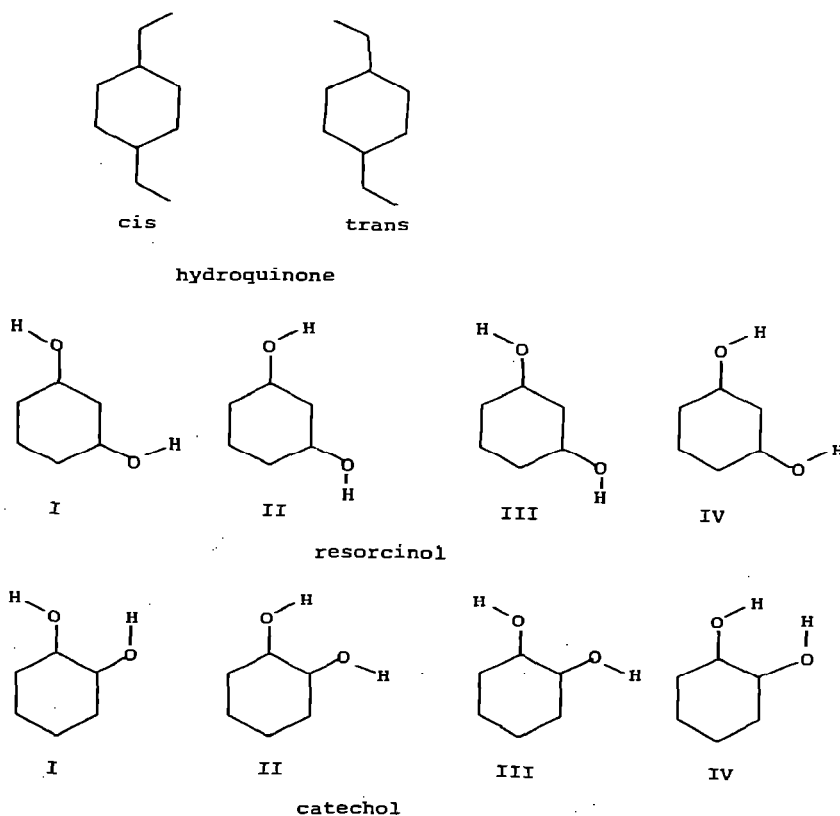


Fig. 2. Structural isomers for the three dihydroxybenzenes.

tions of these two levels are $\approx 2:1$ and we conclude that either the difference in energy between these two species is not large ($\approx 300\text{--}400\text{ cm}^{-1}$) in the ground electronic state and that the barrier between them is also of the order of a few hundred cm^{-1} or else that the barrier is very large and the relative populations simply reflect the ratio of the isomers which were formed upon their synthesis.

The spectrum of phenol has been carefully analyzed and it was concluded [6,7] that the barrier to rotation of the hydrogen out-of-plane motion is $\approx 1000\text{--}1500\text{ cm}^{-1}$ high in the ground state and perhaps as high as $\approx 4500\text{ cm}^{-1}$ in the excited state [7]. Assuming that the para interaction energy is not large, this would imply that the barrier is too high for facile conversion at room temperature but, of course, the possibility of hydrogen-bonded catalysis at the walls or even with other hydroquinone molecules might well reduce this barrier and allow thermal equilibration between the cis and trans forms.

The recent evidence [7–9] supports the calculations by Murrell [10] which favour an enhanced interaction with the benzenoid ring by the para substituents in the lowest electronic excited state of these para-substituted benzene compounds and this suggests that electronic excitation is unlikely to lead to cis–trans interconversion. In fact, the relative stabilities of the ground states of these compounds may be sufficiently different to allow their separation by chromatographic methods.

Recently [11] it has been reported that both meta-substituted phenols and β -naphthol show cis–trans isomerism, with the origin bands being separated by 207 cm^{-1} for the fluorophenol and 318 cm^{-1} for β -naphthol. These authors concluded that the low-frequency origin is cis and the higher origin is of the trans species and they also noted that the intensity of the trans (higher frequency) was larger in both *m*-fluorophenol and β -naphthol, much larger in the latter than the former.

The spectra of catechol and resorcinol are not as clear cut as for hydroquinone. In the spectrum of resorcinol there are two very strong temperature independent bands at 35943 and 36192 cm^{-1} , with the latter being the more intense. As noted above, there is a third, weaker, band at 36166 cm^{-1} which is difficult to assign as the first member of a progression based upon the 35943 cm^{-1} origin since the

Franck–Condon expectation for the second member is far exceeded. Accordingly, we tentatively assign it as the third origin. From fig. 2 it can be seen that, other things being equal (which they almost certainly

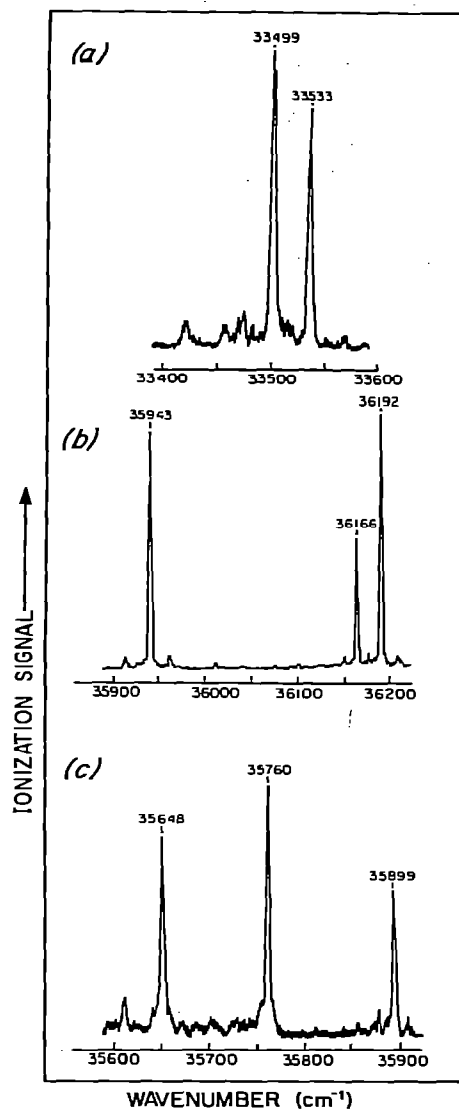


Fig. 3. Resonant two-photon ionization (R2PI) spectra taken in an expansion of 1 atm back pressure of Ar of (a) hydroquinone, (b) resorcinol and (c) catechol. Only the parent molecular ion is monitored in these spectra using a TOF mass spectrometer.

are not), the isomer I, II should have twice the population of the others and, for this reason, we tentatively assign the origin at 36192 cm^{-1} (the strongest) as that for this isomer.

An alternative assignment is suggested by the appearance of the origin at 35943 cm^{-1} since, in all of the jet spectra, it appears to be double, with a splitting of $\approx 2\text{ cm}^{-1}$ which is also the limit of the instrument resolution. This appears less likely than the scheme suggested above since the major splitting is $\approx 250\text{ cm}^{-1}$ and 2 cm^{-1} seems far too small, except by coincidence, to be the difference in transition energy between I(II), III or IV. Also, the totally symmetric progression of 324 cm^{-1} based upon 35943 cm^{-1} does not appear to be double in any of the jet spectra. On this basis, the 2 cm^{-1} splitting must be assigned to the rotational features of the spectrum at low, free jet, temperatures.

In catechol the issue appears to be much more obvious with the temperature independent bands at 35646 cm^{-1} , 35760 cm^{-1} and 35896 cm^{-1} being assigned to the three origins. The band at 35760 cm^{-1} is, indeed roughly twice as intense as the lowest frequency band with the highest frequency band the least intense — as can be seen from fig. 3. As for catechol, there are three isomers (see fig. 2) but it is premature yet to assign which of the bands is to be associated with which isomer. Work is continuing on a more complete assignment of these electronic spectra.

Acknowledgement

DL gratefully acknowledges financial support from a Cottrell Research Grant and the donors of the Petroleum Research Fund, administered by the American Chemical Society. DL also acknowledges support of this work under NSF Grant CHE 83-19383 and partial support from the Army Research Office under Grant DAAG 29-85-K-1005. We thank Chung Hang Sin for technical assistance given during this work.

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