

An ESR study of benzene radical cation in an argon matrix: evidence for favourable stabilization of $^2B_{1g}$ rather than $^2B_{2g}$ state

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Abstract

Benzene radical cations were generated in an argon matrix by fast electron irradiation at 16 K. The ESR spectrum measured immediately after irradiation results probably from the mixture of the two distorted states; however, it converts irreversibly to the spectrum of the $^2B_{1g}$ state upon annealing. The latter spectrum exhibits major hyperfine coupling with four of six protons (the isotropic coupling constant was estimated to be 0.64 mT). The role of basic Jahn–Teller distortion and matrix-assisted effects for benzene radical cations trapped in low-temperature matrices is discussed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The Jahn–Teller distortion of highly symmetrical species manifests itself in optical and magnetic properties, which can be revealed by appropriate spectroscopic techniques [1]. The radical cations of benzene and benzene derivatives are typical Jahn–Teller active species. Detailed information on the vibronic level structure characterizing the Jahn–Teller effect in symmetrically substituted halobenzene radical cations was obtained from classic optical absorption and emission, and, especially, laser-induced fluorescence studies in both gas phase and solid matrices (see, e.g., Refs. [2–7]). Meanwhile, unambiguous identification of the ground state nature for unsubstituted benzene cation is still lacking.

Since $C_6H_6^+$ is a paramagnetic species, low-temperature ESR spectroscopy provides a powerful tool

for elucidation of its electronic structure in solid matrices. Unlike optical spectroscopy, ESR gives no vibrational information; however, the hyperfine coupling parameters are quite sensitive to the structure of SOMO and ground state equilibrium geometry.

The basic Jahn–Teller distortion removes orbital degeneracy of $^2E_{1g}$ state with a D_{6h} symmetry to yield two states with a lower (D_{2h}) symmetry (Fig. 1).

As the spin density distribution in the resulting two states is essentially different, they should be readily distinguishable by ESR. The $^2B_{2g}$ state exhibits major hyperfine coupling with the two equivalent protons at C(1) and C(4), whereas the $^2B_{1g}$ state is characterized by four relatively large equivalent proton couplings corresponding to higher spin density at C(2), C(3), C(5) and C(6) positions. However, the ESR spectrum of benzene radical cation first reported for irradiated benzene adsorbed on silica gel at 77 K [8] revealed hyperfine structure due to six equivalent protons with $a(6H) = 0.44$ mT. Similar

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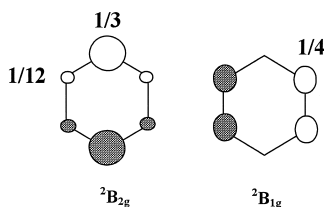


Fig. 1. The structure of SOMOs of the Jahn–Teller states of benzene radical cation. The numbers show spin densities estimated as squares of the Hückel MO coefficients.

results were obtained in other studies of benzene radical cations trapped in silica gels and zeolites, independent of the generation technique used [9–12] (slight g and a anisotropy were noticed [9]). This observation was interpreted as a consequence of dynamic averaging, which occurs for the species trapped in rather large cavities of the hosts used. Although most of these studies were carried out at 77 K or higher temperatures, it was shown [10] that in the cases of a HY molecular sieve and silica gel, averaging occurred down to 3.5 K. This implies that rotation (or pseudorotation) is not frozen even at extremely low temperatures.

In molecular matrices the situation turned out to be quite different. In 1983, Iwasaki et al. reported clear experimental evidence for a static distortion of benzene radical cations trapped in a halocarbon (CFCl_3) matrix [13]. The ESR spectra measured at 4.2–77 K exhibit major hyperfine coupling with two of six protons and marked anisotropic features. This result is consistent with favourable stabilization of the $^2B_{2g}$ state in a CFCl_3 matrix. In this matrix, averaging starts only at ~ 90 K to yield a nearly isotropic septet spectrum with $a(6\text{H}) = 0.432$ mT at 100 K (the spectral changes in the temperature range of 4.2–100 K were found to be fully reversible [13]). Very recently, Kadam et al. gave detailed analysis of the hyperfine coupling constants for benzene radical cations in a CFCl_3 matrix on the basis of ENDOR studies [14]. Their results provide unequivocal support to the earlier interpretation [13]. Furthermore, both experimental data [13,14] are in close agreement with the calculated hyperfine interaction parameters for the $^2B_{2g}$ state [15].

The most important question from the viewpoint of general chemistry is to what extent the results obtained in frozen halocarbon solutions [13,14] re-

flect intrinsic static Jahn–Teller distortion for benzene radical cation. Indeed, the spectra were measured in a strongly interacting solid media with a specific (actually polycrystalline) structure. Therefore, the possibility of dominating matrix assisted effects cannot be excluded. Remarkably, the experimental data reported in [13,14] gave no indications for an admixture of the $^2B_{1g}$ state over the whole temperature range studied. Meanwhile, the theoretical data [12,15,16] are not so conclusive. The calculated energy ordering of the two states depends on the approach used, and the up-to-date level calculations taking into account configuration interaction predict very small difference in the total energy (< 0.5 kcal/mol [12,15]). This means that matrix interactions may affect crucially the stabilization of a specific Jahn–Teller state. Furthermore, there is an experimental indication of possible occurrence of the $^2B_{1g}$ state in the case of monodeuterated benzene on silica gel at 3.5 K [10]. Finally, the relative role of environment and intrinsic structural factors in the shaping of benzene radical cations is unclear.

To the best of our knowledge, benzene radical cations were still not characterized by ESR in a classic matrix isolation experiments, i.e. in deposited solid rare gas matrices. Several approaches for generation of isolated radical cations in rare gas matrices were developed since the 1960s. The results of extensive optical spectroscopic studies of organic cations (including benzene derivatives) in solid argon were reviewed recently [17,18]. Meanwhile, the ESR data for the radical cations resulting from molecules with high ionization potentials in solid rare gases are still quite limited. Knight's group reported the ESR spectra of several small cations trapped in neon [19–21]. Recently, we used fast electron irradiation of deposited rare gas matrices doped with electron scavengers for ESR studies of some larger organic radical cations in argon and xenon [22–24]. In this Letter, we report an application of this technique to the ESR characterization of matrix isolated benzene radical cation.

2. Experimental

A continuous-flow helium cryostat with vacuum resonator was described previously [22,23,25].

Gaseous mixtures were deposited onto a cooled sapphire rod at 18–20 K (in the case of argon) or at 45–50 K (in the case of xenon). The deposited samples were irradiated with fast electrons (1.2 MeV) at 16 K using a Van de Graaff type accelerator EG-2.5 up to the dose of 20 kGy.

The ESR spectra were measured at 8–42 K using an X-band (9.3 GHz) spectrometer with a 100 kHz magnetic field modulation manufactured by SPIN (St. Petersburg, Russia). The low microwave power level (5 μ W) was used in order to avoid signal saturation. High-purity argon (> 99.995%) and xenon (> 99.99%), and reagent grade benzene were used as received. Freon-11 (CFCl_3) and Freon-113 ($\text{CFCl}_2\text{-CF}_2\text{Cl}$) used as electron scavengers were purified by passing through a column packed with Al_2O_3 . Detailed description of the technique used is given elsewhere [22–24].

The computer simulation of powder spectra was carried out using a WinSimfonia program based on a second-order perturbation theory.

3. Results

The ESR spectrum of the benzene/Freon-11/argon system immediately after irradiation at 16 K exhibits a characteristic signal from hydrogen atoms (sharp doublet separated by ~ 51 mT) and a partially resolved multiplet signal centered around $g \approx 2.00$ with the total spread of ~ 3 mT. Although the peak intensity of the doublet signal from H atoms is considerable, double integration shows that the central component strongly predominates in the spectrum (it contributes > 95% into the total integrated intensity). Thus, the hydrogen atoms observed appear to result from some process of minor importance. Similar spectra were also observed with Freon-113 used as an electron scavenger.

Fig. 2 demonstrates the changes in the central signal with annealing and measurement temperature. The irradiated sample was first cooled down to 9 K and then warmed up to different temperatures with the steps of 3–4 K. When the sample temperature rose above the irradiation temperature (16 K), the spectra were also measured at 16 K after each annealing step in order to follow both reversible and irreversible spectral changes.

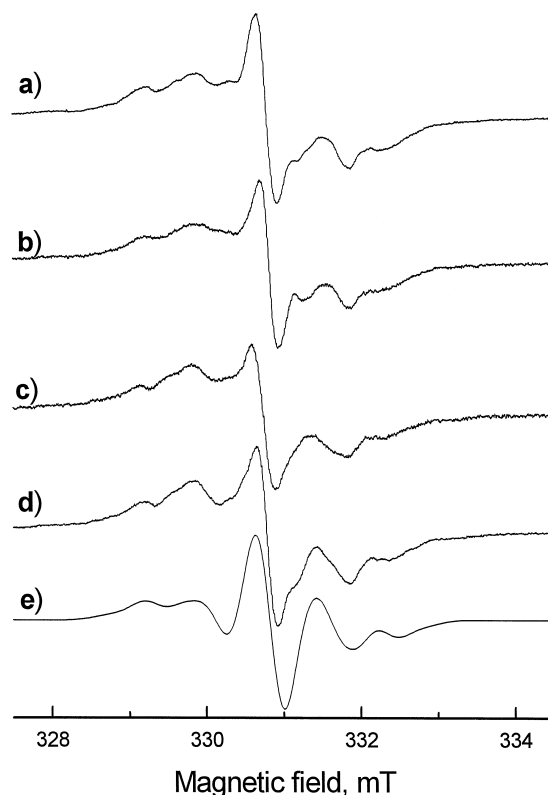


Fig. 2. The temperature dependence of the central region of the ESR spectrum obtained for the system benzene/ CFCl_3 /argon (1:2:1000) irradiated with fast electrons at 16 K. The spectra were measured at different gain at (a) 9, (b) 16, (c) 34 K, and (d) 16 K after annealing at 34 K for 5 min; (e) simulated powder spectrum for the $^2\text{B}_{1g}$ benzene radical cation (see text for the simulation parameters).

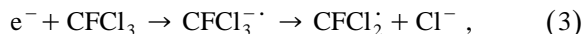
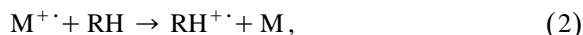
One can see that the spectrum exhibits only slight reversible variations in signal shape below ~ 26 K (Fig. 2a and b). However, at higher temperatures the signal shows certain irreversible changes. Some features observed in the initial spectrum become weaker (or even vanish). As a result, the spectrum measured after annealing the sample at 30–34 K is essentially an anisotropic quintet of non-equidistant lines with an average line separation of ~ 0.7 mT (Fig. 2c and d). The matrix becomes unstable above 39 K, which results in decay of paramagnetic species.

We observed an essentially similar spectral envelope for higher benzene concentrations in an argon matrix; however, the spectrum was broadened, probably, due to the presence of unresolved signal from the dimeric benzene radical cation.

The ESR spectra obtained in a xenon matrix containing benzene and freon scavenger also show the central signal of a similar total spread. However, the structure of this signal is virtually unresolved both at 16 K and at higher temperatures. This poor resolution may be due to line broadening resulting from interaction with matrix magnetic nuclei (^{129}Xe and ^{131}Xe).

4. Discussion

As was shown previously [22–24], in solid rare gas matrices doped with electron scavengers organic radical cations are generated due to positive hole transfer, whereas electrons are trapped chemically, e.g.:



where M represents the matrix atom (e.g., Ar or Xe) and RH is an organic molecule (benzene in the present case). The fluorine-containing radicals resulting from freon give a broad and very weak ESR signal in disordered systems due to large anisotropy of the ^{19}F coupling. Typically, this weak background signal does not affect the spectra of the radical cations under investigation [26], which is one of the most important advantages of using freons as electron scavengers in the ESR studies. The formation of H atoms, which might result from a homolytic C–H bond rupture in neutral excited molecules (products of ion-electron recombination), is strongly suppressed in the presence of electron scavengers. In line with this observation, we did not find noticeable amounts of phenyl radicals¹.

A relatively small total spread of the central signal is characteristic of benzene radical cation. However, the hyperfine structure is essentially different from that reported for the $^2\text{B}_{2g}$ Jahn–Teller distorted state observed in a CFCl_3 matrix [13,14]. Also, the spectrum shows no evidence for a reversible dynamic averaging at elevated temperatures.

The five-line pattern predominating in the spectra of the annealed samples suggests major coupling with four protons, which is qualitatively consistent with the spectrum expected for the $^2\text{B}_{1g}$ state. The magnitude of the observed hyperfine splitting is reasonable for the latter structure. Indeed, the absolute values of isotropic hyperfine proton coupling constants in benzene radical cation are expressed as $a_i = Q\rho_i$, where $Q = 2.59$ mT (as determined from the value of $a_i = 0.432$ mT for six equivalent protons in a dynamically averaged structure) and ρ_i is the spin density at the corresponding carbon atom. In first approximation, the ρ_i values can be estimated from the Hückel MO coefficients (see Fig. 1), that is, for the four protons at C(2,3,5,6) in the $^2\text{B}_{1g}$ structure one has $\rho_i = 0.25$ and $a_i = 0.65$ mT. This value is very close to those obtained in the most accurate up-to-date calculations (0.66 mT [15] and 0.71 mT [12]). The spin density at the other two carbon atoms C(1,4) in the $^2\text{B}_{1g}$ state is negligible (zero in the Hückel approximation or small negative in more sophisticated schemes [12,15]), so the corresponding proton splittings are not resolved.

Although the qualitative interpretation seems to be rather straightforward, it is not so easy to reproduce the shape of real anisotropic signal. We have carried out a series of simulations in order to fit the experimental spectrum. The spectrum shown in Fig. 2e fits the line positions of the observed five non-equidistant components rather well (although the lineshape is not completely reproduced, especially in the low-field region). The hyperfine tensor parameters used in simulation are given in Table 1. An axially symmetrical g tensor similar to that reported by Iwasaki et al. for the $^2\text{B}_{2g}$ state ($g_1 = g_2 = 2.0029$, $g_3 = 2.0023$) was assumed. The theoretical values of dipolar term and isotropic hyperfine constant calculated by Huang and Lunnell [15] are also presented in Table 1 for comparison. One can see that the isotropic hyperfine coupling constant is very close to the calculated value, whereas the dipolar term is somewhat different. Absolute values of the theoretical dipolar contributions [15] appear to be larger than the experimental constants estimated from simulation; similar trend was proved for the $^2\text{B}_{2g}$ state characterized in a CFCl_3 matrix [13,14]. However, we should note that the agreement between simulated and experimental spectra is, at best, rea-

¹ A well-resolved ESR spectrum of phenyl radical in an argon matrix was reported by Kasai et al. [27]. It can be easily detected in the system under study because of larger total spread.

Table 1

Parameters of the hyperfine coupling tensor for the $^2B_{1g}$ benzene radical cation used in simulation

	Hyperfine tensor for H(2, 3, 5, 6) (mT)	Dipolar term (mT)	Principal direction cosines		
			X	Y	Z
A_1	−0.93	−0.29 (−0.41)	±0.5	0.8667	0
A_2	−0.3	+0.34 (+0.51)	−0.8667	±0.5	0
A_3	−0.69	−0.05 (−0.1)	0	0	1
a_{iso}	−0.64 (−0.66)				

The values in parentheses show the coupling parameters calculated by Huang and Lunell [15].

sonable. Thus, we consider the values given in Table 1 only as first estimates. As was mentioned above, the hyperfine coupling parameters for the protons at C(1) and C(4) are expected to be small for the $^2B_{1g}$ state (the calculated isotropic hyperfine constant is 0.1 mT [15]), so the signal shape is rather insensitive to these parameters (note that the experimental linewidth is ~ 0.3 mT).

The precise shape of the additional signal observed in the ESR spectra measured at low temperatures cannot be established unambiguously because of strong overlapping of the spectra. However, most probably, this signal should result from the admixture of the other state of benzene radical cation, i.e., $^2B_{2g}$ state, which appears to be less stable in an argon matrix. No attempts were made to fit the experimental spectrum by simulation because the number of variable parameters (including hyperfine couplings, lineshape parameters and component ratio) appears to be too large, and the experimental spectrum is not resolved enough. Nevertheless, we may note that small splittings of the central line probably result from relatively small couplings with four protons at C(2, 3, 5, 6) in the $^2B_{2g}$ structure. It is possible that an admixture of the $^2B_{2g}$ state also contributes, to a certain extent, into the spectra of annealed samples. However, this contribution becomes smaller with increasing the annealing temperature. Since the total integrated intensity of the signal from benzene radical cations measured at 16 K remains unchanged upon annealing (at least, up to 34 K), we can conclude that the $^2B_{2g}$ state converts irreversibly to the more stable $^2B_{1g}$ state at elevated temperatures. This conversion is probably due to the trapping site relaxation in an argon matrix. Note that we observed no dynamic averaging due to rotation (or pseudorotation) in the whole temperature range studied.

The results obtained in the present work seem to be rather unexpected in view of previous studies of the structure and dynamics of benzene radical cations. Indeed, the energy ordering of the two Jahn–Teller states revealed in our studies is opposite to that observed in a $CFCI_3$ matrix [13,14]. However, this may be not so surprising if we take into account the very small difference in energy of isolated states. It is quite clear that cation–matrix interactions and trap structure should play a very important role in determining the specific state of benzene cation stabilized in the matrix. In particular, strong preference of the $^2B_{2g}$ state in a $CFCI_3$ matrix may be due to specific matrix interactions rather than to intrinsic factors. Also to be mentioned, we have an indication of the presence of both two states immediately after ionization in an argon matrix. Two different forms of benzene radical cations are probably stabilized in different trapping sites, one of those is more stable (relaxed). In general, the argon matrix appears to be more suitable for the studies of basic structural effects since argon atoms are low-polarizable and spherically symmetrical (unlike the freon molecules). From this point of view, it seems better to use an argon matrix study as experimental test for theoretical predictions concerning the Jahn–Teller effect. However, the matrix effects can be significant even for argon, and at present it is difficult to say whether the relative stability of the two Jahn–Teller states in argon actually reflects the basic distortion. More experimental and theoretical work should be done.

5. Conclusions

The ESR studies of benzene radical cations under rigorous matrix isolation conditions indicate favourable stabilization of the $^2B_{1g}$ state rather than the

$^2B_{2g}$ state, in contrast to the previous results for freon matrices. This dramatic matrix effect can be understood taking into account the very small differences in the total energy of the states under consideration. Although an intrinsic instability of symmetrical benzene radical cation is caused by the Jahn–Teller effect, matrix effects may determine selective stabilization of a specific distorted state to a large extent. A remarkable structural flexibility of the benzene radical cation provides a unique possibility for experimental and theoretical studies of the relationship between basic Jahn–Teller distortion and matrix-assisted effects. In particular, it would be of interest to characterize the ESR spectra of specific isotopomers of the D_{2h} benzene radical cation, which should have larger separation between the energy levels. On the other hand, it would be worthwhile to follow the structure of benzene radical cations trapped in the solid rare gas matrices with various ‘electronic rigidity’ (polarizability). The studies in these directions are in progress now.

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