Jahn-Teller instability in $C_6H_6^+$ and $C_6H_6^-$ revisited.

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The benzene cation ($C_6H_6^+$) has a doublet (e_{1g}) ground state in hexagonal ring (D_{6h} geometry. Therefore a Jahn-Teller (JT) distortion will lower the energy. Theoretical quantum chemistry calculations suggest a value 4-5 times larger than the value deduced from the recent high-resolution photoionization measurements by Linder *et al.* Specifically, they measured the frequency shift of the e_{2g} in-plane ring-bending vibrational mode, and their analysis gives a JT energy reduction of 208 cm^{-1}. The present theoretical study yields a model Hamiltonian that includes the JT coupling of the e_{1g} electronic ground state with the *two* e_{2g} vibrational modes: in-plane ring-bending and C-C bond-stretching. We obtain the JT couplings from density functional theory (DFT), which gives a JT energy lowering of 970 cm^{-1}. Our model reconciles the experimental finding of Linder *et al.* and theoretical calculations of the present and previous studies. We predict frequencies shifts of both the benzene cation and anion, and give a reinterpretation of the available experimental data.

A molecular system with a degenerate electronic ground state will spontaneously lower its symmetry to lift the degeneracy. This is the Jahn-Teller (JT) [1] effect, and is common in molecules [2]. The C_6H_6 (benzene) molecule has a long history of study [3]. With full D_{6h} symmetry, the highest occupied molecular orbital (HOMO) e_{1g} is doubly degenerate, as is the lowest unoccupied molecular orbital (LUMO) e_{2u}. Hence both the cation and anion are JT unstable and prefer lower symmetry. In the lowest (linear) approximation, the Born-Oppenheimer surface has a degenerate loop in configuration space surrounding the D_{6h} ground state. Everywhere on this loop, the HOMO and LUMO states are split by a constant JT gap. The most symmetric points on this loop represent simple D_{2h} distortions. These distortions occur in three equivalent "acute" and three equivalent "obtuse" forms (see the inset to Fig. 2). Higher order corrections lift the degeneracy on the loop, but zero-point energy exceeds the barrier height, creating a dynamic rather than a static JT distortion.

Ab initio approaches [4–6] including density functional theory (DFT) [7,8] have been used to predict the ground state geometry and the JT energy lowering in the benzene cation. A high resolution zero-kinetic-energy (ZEKE) photoelectron study by Linder *et al.* [9] found values of the frequency shift of the in-plane ring-bending e_{2g} vibrational mode. From their analysis, they deduced the JT energy lowering to be 208 cm^{-1}. They also concluded that the cation has a global minimum for the acute D_{2h} geometry, with a local minimum for the obtuse geometry only 8 cm^{-1} higher in energy. *Ab initio* calculations [6] suggest 4-5 times greater energy gain. The present study reconciles this discrepancy. We provide a microscopic model Hamiltonian for the π-electron system, which includes two independent e_{2g} modes of JT coupling. We derive all parameters of this model from new DFT calculations. Our revised theory gives vibrational spectra for both the cation and anion. Our results for the anion permit a reinterpretation of the ZEKE spectra, allowing a larger JT energy lowering, which agrees with both our DFT and previous theory.

The starting point is a Hückel-type Hamiltonian for the π electrons, with a first-neighbor hopping integral $t_1 = - < i|\mathcal{H}|i \pm 1 >$ between adjacent p_z atomic orbitals on the six C atoms. In Slater-Koster notation [10], $-t_1$ is called the $(pp\pi)$ two-site integral. In the D_{6h} point group, all six t_1 integrals are the same. The 6-dimensional electronic Hilbert space has single-particle states with a_{2u}, e_{1g}, e_{2u}, b_{1g} symmetries, which have energies $-2t_1, -t_1, t_1, 2t_1$.

Hopping matrix elements t decrease with distance between atoms. For small atomic displacements, t depends linearly on the C-C bond length, $t_1(\delta R_{i,i+1}) = t_1^0 - g_1 \delta R_{i,i+1}$. The electron-phonon coupling constant g_1 is the same as in the Su-Schriefer-Heeger model [11] for polyacetylene. Next we introduce second neighbor hopping $t_2 =< i-1|H|i+1 >= t_2^0 + g_2 \delta\alpha_i$ to include a dependence on the change $\delta\alpha_i$ of the C_{i-1}-C_i-C_{i+1} bond angle α_i from 120°. The constant term t_2^0 does not lift the degeneracy of the e levels. Therefore we put $t_2^0 = 0$ to keep the Hamiltonian as simple as possible. We use harmonic restoring forces K_1, K_2 for the bond stretching and angle bending vibrations. The total Hamiltonian $\mathcal{H} = \mathcal{H}_{\rm el} + \mathcal{H}_{\rm vib}$ has the form

$$\begin{aligned}\mathcal{H}_{\rm el} &= \sum_{i=1}^{6} \left[-t_1^0 + g_1 \delta R_{i,i+1} |i><i+1| \right.\\ &\quad \left. + g_2 \delta\alpha_i |i-1><i+1| + h.c.\right]\\ \mathcal{H}_{\rm vib} &= \sum_{i=1}^{6} (P_i^2/2M + K_1 \delta R_{i,i+1}^2/2 + K_2 \delta\alpha_i^2/2).\end{aligned} \tag{1}$$

The coupling constants $g_{1,2}$ and spring constants $K_{1,2}$ are calculated from DFT using the program NRLMOL [12] with a Gaussian basis set and the Perdew-Burke-Ernzerhof exchange-correlation potential [13]. This yields as the optimal geometry of neutral benzene in D_{6h} symmetry, the C-C and C-H bond lengths of 1.398 Å and 1.08 Å respectively. The energy difference between the HOMO e_{2g} and a_{2u} orbitals defines the hopping integral $t_1^0 = 2.72$ eV. We fix the C-H bond length and introduce a symmetric a_{1g} breathing distortion, which alters the C-C bond lengths. The results, shown on Fig. (1), can be fitted to the predictions of the model Hamiltonian (1) $E = E_0 + 3K_1\delta R^2$ (for the total energy) and $\Delta E = t_1 = t_1^0 - g_1\delta R$ for the $E(e_{1g}) - E(a_{2u})$ eigenvalue difference. The results are $g_1 = 5.27$ eV$/\mathring{A}$ and $K_1 = 47.4$ eV$/\mathring{A}^2$.

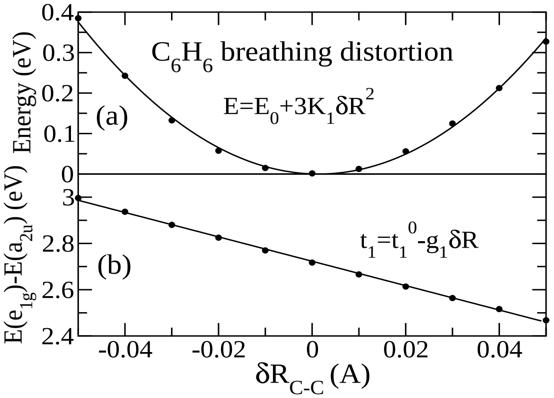

FIG. 1. (a) DFT total energy for neutral benzene with a symmetric a_{1g} distortion around the equilibrium C-C separation (closed circles). (b) Eigenvalue difference for the two lowest π states (closed circles). The C-H bond lengths are held fixed for both calculations. The solid curves are best fits using the model Hamiltonian Eq. (1) with g_1 and K_1 adjusted.

Second neighbor integrals are found from DFT energies for distortions with D_{2h} symmetry. We fixed the C-C bond lengths and varied the bond angle $\delta\alpha$ as shown in the inset to Fig. (2). Specifically, angles 1 and 4 were decreased by 2α, while the remaining four angles were increased by α. The hydrogen atoms were fixed along the bisectors of the C-C-C angles. The results were fitted to the predictions of the Hamiltonian (1) $E = E_0 + 6K_2\delta\alpha^2$ for the total energy, and $4g_2\delta\alpha$ for the splitting of doubly degenerate e_{1g} HOMO states into b_{2g} and b_{3g} singlets. The results are $K_2 = 7.45$ eV/rad^2 and $g_2 = 0.91$ eV/rad.

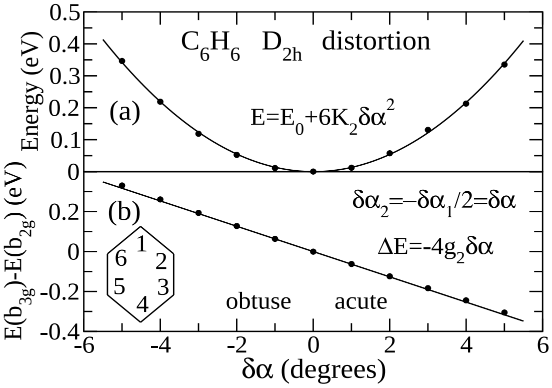

FIG. 2. (a) DFT total energies and (b) splitting of the doublet HOMO eigenvalues of neutral benzene with a D_{2h} distortion and fixed C-C bond lengths as shown in the inset. The solid curves are best fits using the model Hamiltonian Eq. (1) to fix the parameters g_2 and K_2.

For fixed atomic coordinates, the adiabatic potential energy surface (APES) can easily be calculated using Eq. (1). For the D_{2h} distortion shown in the inset of Fig. (2), the energy depends on three variables $\delta R_1 = \delta R_{12}$, $\delta R_2 = \delta R_{23}$ and $\delta\alpha_2 = -\delta\alpha_1/2 = \delta\alpha$. The electronic contribution is the sum of the occupied eigenvalues of Eq. (1), taking into account the spin degeneracy,

$$
\begin{aligned}
E_{\rm el}^{<}(\mathrm{C_6H_6^+}) &= -7t_1^0 + g_1(4\delta R_1 + 3\delta R_2) + 2g_2\delta\alpha \\
E_{\rm el}^{>}(\mathrm{C_6H_6^+}) &= -7t_1^0 + \frac{g_1}{3}(16\delta R_1 + 5\delta R_2) - 2g_2\delta\alpha \\
E_{\rm el}^{<}(\mathrm{C_6H_6^-}) &= -7t_1^0 + \frac{g_1}{3}(16\delta R_1 + 5\delta R_2) + 2g_2\delta\alpha \\
E_{\rm el}^{>}(\mathrm{C_6H_6^-}) &= -7t_1^0 + g_1(4\delta R_1 + 3\delta R_2) - 2g_2\delta\alpha \\
E_{\rm vib} &= K_1\left(2\delta R_1^2 + \delta R_2^2\right) - \frac{8g_1}{3}\left(2\delta R_1 + \delta R_2\right) + 6K_2\delta\alpha^2 \qquad (2)
\end{aligned}
$$

The energy is not analytic at the point $(\delta R_1, \delta R_2, \delta\alpha)$=(0,0,0), but has a cusp, characteristic of the first-order JT splitting. Therefore there are separate expressions in Eq. (2), $E_{\rm el}^{<}$ and $E_{\rm el}^{>}$ for the branches corresponding to acute ($\delta\alpha < 0$) and obtuse ($\delta\alpha > 0$) geometries. Only electronic terms linear in displacements are kept. The vibrational contribution $\mathcal{H}_{\rm vib}$ does not depend on the electronic configuration and is minimum at the neutral benzene coordinates.

Charged benzene lowers its energy by $\delta E_1 + \delta E_2 + \delta E_3$ corresponding to atomic relaxation *via* three types of vibrational modes. The first is the symmetric A_{1g} distortion of D_{6h} symmetry, $\delta R_1 = \delta R_2 = \delta R_0$ and $\delta\alpha = 0$. From Eq. (2) the optimal displacements and energy shift are $\delta R_0 = g_1/6K_1 = 0.018$Å and $\delta E_1 = -g_1^2/12K_1 = -49$meV for both cation and anion. There are two E_{2g} vibrational modes. These are the only vibrations which can lift the degeneracy of the HOMO and LUMO orbitals. In our full treatment, these are described by four vibrational amplitudes, but for simplicity of presentation, we show only the two partners which give rise to D_{2h} symmetry. The two degenerate minima that we will find are just two points on a closed path in the full 4-dimensional space of E_{2g} distortions.

The ring-bending mode gains energy $\delta E_2 = -g_2^2/6K_2 = -19$meV at optimal $\delta\alpha = \pm g_2/6K_2 = \pm 1.2°$ for both charged molecules with acute and obtuse geometries respectively. The largest contribution to the energy relaxation comes from the C-C bond-length distortion. It is more convenient to measure distortions $\delta R'$ around the relaxed breathing positions $R = R_0 + \delta R_0 = 1.416$ Å. The energy gain due to the C-C bond-length symmetry breaking distortion is $\delta E_3 = -g_1^2/6K_1 = -98$ meV for $\delta R_2' = -2\delta R_1' = \pm g_1/3K_1 = \pm 0.037$ Å in acute and obtuse geometries respectively. The linearized Eq. (2) gives degenerate ground state energies for acute and obtuse geometries. The non-linearized Eq. (1) contains quadratic JT coupling $b = g_1^2/9K_1t_1^0$, which breaks the symmetry between the acute and obtuse geometries predicting $\delta R_2' = g_1/3K_1(1-4b)^{-1} = 0.041$Å ($\delta R_2' = -g_1/3K_1(1-3b)^{-1} = -0.040$Å) for acute (obtuse) geometries. Thus this model predicts the acute distortion to be the global minimum, lower by $b/(1-7b)g^2/6K_1 \sim$3meV than the obtuse local minimum. The total JT energy lowering is 0.127 (0.124) eV; the JT gap splitting the orbitals is 0.511 (0.491) eV, for acute (obtuse) geometries.

Let us compare the model Hamiltonian results with the true DFT answer. For the a_{1g} breathing mode the optimal carbon distortions are $\delta R_0^{\rm DFT} = 0.014$ (0.022) Å and the relaxation energies are $\delta E_1^{\rm DFT} = 28$ (46) meV for $\mathrm{C_6H_6^+}$ ($\mathrm{C_6H_6^-}$) respectively. The fully relaxed D_{2h} minimum in $\mathrm{C_6H_6^+}$ for the obtuse geometry is predicted at $\delta R'_2 = -0.039$ Å, $\delta R'_1 = 0.019$ Å, $\delta\alpha = -1.28°$. The JT energy lowering and the HOMO splitting are δe_{tot} = -0.125 eV and $2\Delta = 0.530$ eV respectively. The acute minimum at $\delta R'_2 = 0.043$ Å, $\delta R'_1 = -0.019$ Å, $\delta\alpha = -0.87°$ has JT energy lowering and HOMO splitting of -0.117 eV and 0.481 eV respectively. The energy difference (8 meV) found between the acute or obtuse distortions is sensitive to the choice of exchange-correlation potential and smaller than the errors of calculations [7]. The geometry and energies of the DFT solution are reasonably well reproduced by the model Hamiltonian. The DFT energy lowering and carbon atomic distortions are affected by hydrogen distortions as well, which are left out completely in Eq. (1). The model Hamiltonian also predicts the same energy lowering for the cation and anion. Use of a non-zero second neighbor integral $t_2^0 \neq 0$ causes electron-hole symmetry to be broken. The main conclusion is that the C-C bond-length distortions contribute the most to the JT energy lowering and degenerate level splitting in both the benzene cation and anion.

JT-coupled vibrational modes change their frequencies on a charged molecule. The observable frequency shifts serve as a measure of the JT energy lowering. We solve the model Hamiltonian for the vibrational spectra for both cation and anion. For the case of the cation, the Hamiltonian (1) is projected on the two e_{1g} HOMO states with symmetries b_{3g} and b_{2g} in the D_{2h} point group,

$$\begin{aligned} |b_{3g}> &= \frac{1}{\sqrt{12}}\left(2|1> + |2> - |3> - 2|4> - |5> + |6>\right) \\ |b_{2g}> &= \frac{1}{2}\left(|2> + |3> - |5> - |6>\right) \end{aligned} \tag{3}$$

The Hamiltonian takes form $H = H_0\hat{I} + H_3\sigma_3 + H_x\sigma_x$, where σ_β are the Pauli matrices in the $\{b_{3g}, b_{2g}\}$ subspace,

$$\begin{aligned} \mathcal{H}_0 &= \sum_{i=1}^{6}\left(P_i^2/2M + K_1\delta R'^2_{i,i+1}/2 + K_2\delta\alpha_i^2/2\right) \\ \mathcal{H}_3 &= \frac{g_1}{6}(\delta R'_1 + \delta R'_3 + \delta R'_4 + \delta R'_6 - 2\delta R'_2 - 2\delta R'_5) \\ &+ \frac{g_2}{2}(\delta\alpha_1 + \delta\alpha_4) \\ \mathcal{H}_x &= \frac{g_1}{\sqrt{12}}(\delta R'_1 - \delta R'_3 + \delta R'_4 - \delta R'_6) \\ &+ \frac{g_2}{\sqrt{12}}(\delta\alpha_2 - \delta\alpha_3 + \delta\alpha_5 - \delta\alpha_6) \end{aligned} \tag{4}$$

In adiabatic approximation, the JT orbital splitting is $2\Delta = 2g_1^2/3K_1 + 2g_2^2/3K_2$ and the JT energy lowering is $E_{\text{JT}} = -\Delta/2$. To solve the problem beyond the adiabatic approximation we have to quantize vibrational motions in Hamiltonian (4). In Cartesian coordinates $(\delta x_i, \delta y_i)$ the kinetic energy term is diagonal and the potential energy depends on a single parameter $K_2/K_1R^2 = \Lambda$. For $\Lambda = 0.0784$ and total mass $M = M_C + M_H$ we get nine normal modes: the ring bending E_{2g} mode at $\omega_1 = 581$ cm^{-1} with some admixture of the C-C bond length alteration, the pure ring bending B_{1u} mode at 962 cm^{-1}, the breathing A_{1g} mode at 992 cm^{-1}, the mostly C-C bond-length-alteration modes E_{1u} and E_{2g} at 1262 cm^{-1} and $\omega_2 = 1644$ cm^{-1} and the pure C-C bond-stretching mode B_{2u} at 1718 cm^{-1}.

Using the DFT NRLMOL code we calculated all benzene normal modes and compared them with the model Hamiltonian result. There are 21 in-plane vibrational modes $\Gamma = 2A_{1g} + A_{2g} + 4E_{2g} + 2B_{1u} + 2B_{2u} + 3E_{1u}$. Six of them are high frequency C-H modes $A_{1g} + B_{1u} + E_{1u} + E_{2g}$ around 3100 cm^{-1}. From the remaining 15 vibrations we identify the ring-bending E_{2g} mode at 600 cm^{-1}, the breathing A_{1g} at 992 cm^{-1}, and the bond-stretching E_{2g} at 1589 cm^{-1}. Both E_{2g} vibrational modes lift the degeneracy of the e$_{1g}$ HOMO orbital. The Hamiltonian (4) in terms of normal coordinates $\Theta_{i=1..12}$ has the form

$$\begin{aligned} \mathcal{H}_0 &= \frac{M}{2}\left(\dot\Theta_1^2 + \dot\Theta_2^2 + \omega_1^2\left(\Theta_1^2 + \Theta_2^2\right)\right) \\ &+ \frac{M}{2}\left(\dot\Theta_3^2 + \dot\Theta_4^2 + \omega_2^2\left(\Theta_3^2 + \Theta_4^2\right)\right) \\ \mathcal{H}_3 &= -G_1\left(\Theta_1\cos(\beta_1) - \Theta_2\sin(\beta_1)\right) \\ &\quad -G_2\left(\Theta_3\cos(\beta_2) - \Theta_4\sin(\beta_2)\right) \\ \mathcal{H}_x &= -G_1\left(\Theta_1\sin(\beta_1) + \Theta_2\cos(\beta_1)\right) \\ &\quad +G_2\left(\Theta_3\sin(\beta_2) + \Theta_4\cos(\beta_2)\right), \end{aligned} \tag{5}$$

where the electron-phonon coupling constants $G_1 = T_1 g_1/6 + T_2 g_2/2R_0 = 1.3$ eV/Å and $G_2 = T_3 g_1/6 - T_4 g_2/2R_0 = 4.14$ eV/Å are non-zero only for the two in-plane vibrational E_{2g} modes, Θ_1, Θ_2 are the ring bending modes and Θ_3, Θ_4 are the bond-streatching modes. The constants $T_1 = 0.647$, $T_2 = 2.288$, $T_3 = 5.439$, and $T_4 = 2.183$ depend on Λ and the form of $\mathcal{H}_0$ in Eq. (4). The phases $\beta_{1,2}$ are arbitrary and define the basis for two e_{1g} modes. However, rotation of the electronic subspace Eq. 3 by angle α transforms the Hamiltonian (5) to $\mathcal{H}' = U^\dagger \mathcal{H} U$, where U is a rotation matrix in e_{1g} space by angle α. The transformed Hamiltonian $\mathcal{H}'$ has the same form as Eq. (5) with phases $\beta_1' = \beta_1 + 2\alpha$ and $\beta_2' = \beta_2 - 2\alpha$. When $\alpha = \pm\pi$ the electronic wavefunction changes sign whereas the vibrational coordinates completes the circuit. The phase acquired by a quantum system moving adiabatically around the circuit in the parameter space of the system is called a "Berry phase" [14]. This phase is $\alpha = (\delta\beta_1 - \delta\beta_2)/4$ in Eq. (5).

To solve Eq. (5) for the vibrational spectrum, assume for the moment a zero coupling to the bond stretching vibrational mode $G_2 = 0$. Then Eq. (5) depends on a single parameter $\kappa_1 = (\Delta_1/\hbar\omega_1)^{1/2} = 1.18$, where $\Delta_1 = G_1^2/M\omega_1^2 = 817\mathrm{cm}^{-1}$ is the twice the JT energy gain due to the ring-bending mode. We seek the solution of Eq. (5) in the form

$$|\Psi> = \sum_{n_1=0}^{N} \sum_{n_2=0}^{N-n_1} \left[A_{n_1,n_2} \frac{(a_1^\dagger)^{n_1}}{\sqrt{n_1!}} \frac{(a_2^\dagger)^{n_2}}{\sqrt{n_2!}} |0> |b_{3g}> \right.$$
$$\left. + B_{n_1,n_2} \frac{(b_1^\dagger)^{n_1}}{\sqrt{n_1!}} \frac{(b_2^\dagger)^{n_2}}{\sqrt{n_2!}} |0> |b_{2g}> \right] \tag{6}$$

The electronic basis functions are chosen to make the $\mathcal{H}_0 \hat{I}$ diagonal. The operators $a_{1,2}^\dagger$, $b_{1,2}^\dagger$ create harmonic oscillator states in the two-dimensional manifold of e_g vibrations, with their origin at the symmetric (D_{6h}) benzene ion coordinates. Although different from the basis of Longuet-Higgins et. al. [3], who used polar coordinates, both basis sets are complete and converge rapidly to the same solution. The solution is found by exact diagonalization of Eq. (5) for $N = 10$. The eigenvalues coincides with those of Linder et. al. [9] (Fig. 3) for the case of the zero quadratic coupling.

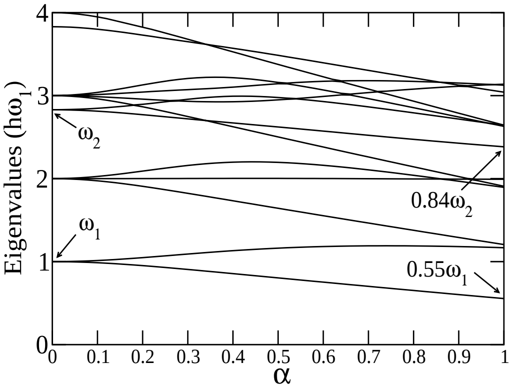

FIG. 3. Vibrational spectrum of the Jahn-Teller unstable ion *versus* parameter α, where coupling constants $\kappa_1 = 1.18 * \alpha$ and $\kappa_2 = 0.8 * \alpha$. For the cation, the coupling constant for the ring bending mode is $\kappa_1 = 1.18$ and coupling to the bond stretching mode is $\kappa_2 = 0.8$. Therefore for $\alpha = 1$ the neutral molecule vibrational frequency $\omega_1 = 581$ cm^{-1} becomes $0.55\omega_1$ and $\omega_2 = 1644$ cm^{-1} reduces to $0.84\omega_2$ for the cation.

The vibrational frequencies on the neutral molecule $\omega_1 = 581$ cm^{-1} and $\omega_2 = 1644$ cm^{-1} become (for the benzene cation) $0.54\omega_1$ (for $\kappa_1 = 1.18$ and $G_2 = 0$) and $0.7\omega_2$ (for $\kappa_2 = 0.8$ and $G_1 = 0$). To take into account the interaction between the two E_{2g} vibrational modes (when both $G_1 \neq 0$ and $G_2 \neq 0$) one has to use a trial wavefunction similar to Eq. (6), but including all four vibrational modes. The size of the matrix grows as $2 \times C_{N+4}^4 \approx (N + 2.5)^4/12$. Convergence was reached for $N = 10$. The lowest eigenvalues as a function of parameter α are shown on Fig. 3. The coupling constants are proportional to α and at $\alpha = 1$ they become $\kappa_1 = 1.18$ and $\kappa_2 = 0.8$. The frequency shift of the ring bending mode $\omega_1 \to 0.55\omega_1$ is essentially the same as in the noninteracting case. The interaction of the bond stretching mode with the ring bending overtones results in the level repulsion, such that $\omega_2 \to 0.84\omega_2$ for $\kappa_2 = 0.8$. The predicted vibrational spectrum corresponds to $\alpha = 1$ on Fig. 3.

On the anion, a D_{2h} distortion splits the e_{2u} LUMO into two b_{1u} and a_u orbitals, which can be obtained from Eq. (3) by changing the sign in front of the $|2>$, $|4>$, $|6>$ molecular orbitals. Projecting the Hamiltonian Eq. (1) into the $\{b_{1u}, a_u\}$ manifold leads to the same Hamiltonian as (5) with a sign change of coupling constant $g_1 \to -g_1$. The vibrational excitation spectra on anion $C_6H_6^-$ is described by Eq. (6), with coupling constants $G'_1 = -T_1g_1/6+T_2g_2/2R_0 = 0.17$ eV/Å and $G'_2 = -T_3g_1/6-T_4g_2/2R_0 = -5.48$ eV/Å. The JT energy lowering on the anion is the same as for the cation $G'^2_1/M\omega_1^2 + G'^2_2/M\omega_2^2 = 0.234$ eV, but the effective couplings to the ring bending and C-C bond stretching modes are now different; $\kappa'_1 = 0.16$ and $\kappa'_2 = 1.06$ respectively. This means that the frequency of the ring bending E_{2g} mode is shifted by less then 2% from the neutral benzene value, whereas the bond-stretching E_{2g} mode becomes 59% of the neutral molecule value 1644 cm^{-1}.

Using the model Hamiltonian Eq. (1) with DFT-calculated parameters, we predict the JT stabilization energy of 944 cm^{-1} for both the benzene cation and anion. The bond-stretching mode 1644 cm^{-1} on neutral benzene experiences a large shift on the anion and becomes 970 cm^{-1}, which is very close in energy to the a_{1g} breathing mode 992cm^{-1}. On the other hand, the ring-bending mode is essentially unaffected. To the contrary, on the cation both E_{2g} JT active modes experience the sizable shifts by 46% and 30% from their neutral benzene values. Experimentally [9,15] the ring-bending mode on the benzene cation was measured to reduce from 536cm^{-1} to 350cm^{-1} (or by 35%). This measurements led Linder *et al.* [9] to deduce a JT energy stabilization of 208 cm^{-1}. A more detailed analysis, including quadratic JT coupling, led to the conclusion that the acute D_{2h} distorted geometry is the global minimum, lower by 8 cm^{-1} than the obtuse local minimum. Our Hamiltonian (5) predicts a larger shift of the ring bending mode by 11%. The amount of the shift is sensitive to the choice of normal modes determined by the term $\mathcal{H}_0$ Eq. (5), a slightly oversimplified model. The main result of our new solution is that there are **two** contributions to the JT energy lowering. To determine the JT energy lowering on the cation **two** vibrational E_{2g} frequencies have to be measured. The model Hamiltonian (1) contains quadratic couplings, which predict an acute global minimum, while the accuracy of the true DFT answer is insufficient to make such a prediction [7].

The benzene anion is not stable, which makes it difficult to measure the vibrational spectrum. Electron transmission techniques [16] give an opportunity to measure the vibrational sidebands in the resonant electron cross section at negative electron affinity energy 1.1 eV [16]. The spectrum shows vibrational peaks separated by 123 meV (or 992 cm^{-1}), and were attributed to a_{1g} vibrational quanta. The higher frequency JT-active e_{2g} mode has not been resolved. Our results, however, suggest that since both breathing and C-C bond stretching modes are coupled to the LUMO, a mixture of the two is expected to be present in the spectrum. Since the e_{2g} modes becomes very close in energy to the breathing a_{1g} mode, it is difficult to distinguish experimentally between the two.

In conclusion we derived a new model Hamiltonian for the JT active benzene cation and anion, and obtained all parameters from DFT calculations. This model Hamiltonian predicts a JT stabilization energy of 970 cm^{-1}. This value, similar to other first-principles results, is 4.5 times larger than the value deduced experimentally by Linder *et al.* [9]. However, our model gives the result that **two** E_{2g} modes are JT-active, coupling to the electronic HOMO and LUMO states. Only one of them was measured [9], and our results are reasonably consistent with that measurement. However, both modes are needed to obtain the JT stabilization energy from spectroscopic data. We conclude that there is no contradiction between theory and experiment, and predict the relevant frequency shifts that can be used to test theory more completely.

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[1] H. Jahn and E. Teller, Phys. Rev. **49**, 874 (1936).

[2] I. B. Bersuker, Chem. Rev. **101**, 1067 (2001); T. A. Barckholtz and T. A. Miller, Int'l Rev. Phys. Chem. **17**, 435 (1998).

[3] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, Sack R. A., Proc. R. Soc. London, Ser. A **244**, 1 (1958).
[4] M. Engström, O. Vahtras, and H. Agren, Chem. Phys. **243**, 263 (1999).
[5] H. Köppel, L. S. Cederbaum, and W. Domcke, J. Chem. Phys. **89**, 2023 (1988).
[6] K. Raghavachari, R. C. Haddon, T. A. Miller, and V. E. Bondybey, J. Chem. Phys. **79**, 1387 (1983).
[7] K. Muller-Dethlefs and J. B. Peel, J. Chem. Phys. **111**, 10550 (1999).
[8] K. Yoshizawa, T. Kato, and T. Yamabe, J. Chem. Phys. **108**, 7637 (1998).
[9] R. Linder, K. Müller-Dethlefs, E. Wedum, K. Haber, E. R. Grant, Science **271**, 1698 (1996).
[10] J. C. Slater and G. D. Koster, Phys. Rev. **94**, 1498 (1954).
[11] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).
[12] M. R. Pederson and K. A. Jackson, Phys. Rev. B. **41**, 7453 (1990); K. A. Jackson and M. R. Pederson, Phys. Rev. B. **42**, 3276 (1990); M. R. Pederson and K. A. Jackson, Phys. Rev. B. **43**, 7312 (1991); D. V. Porezag and M. R. Pederson, Phys. Rev. B. **54**, 7830 (1996); A. Briley, M. R. Pederson, K. A. Jackson, D. C. Patton, and D. V. Porezag, Phys. Rev. B. **58**, 1786 (1998).
[13] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[14] M. V. Berry, Proc. R. Soc. London Ser. A **392**, 45 (1984).
[15] J. G. Goode, J. D. Hofstein, and P. M. Johnson, J. Chem. Phys. **107**, 1703 (1997).
[16] P. D. Burrow, J. A. Michejda, K. D. Jordan, J. Chem. Phys. **86**, 9 (1987).