

The Jahn-Teller and pseudo-Jahn-Teller effects in propyne radical cation

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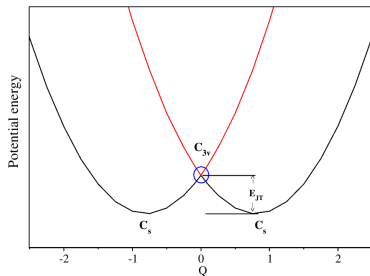
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The Jahn-Teller theorem

- "... stability and degeneracy are not possible simultaneously unless the molecule is a linear one ..." ¹
- Structural aspects, global minimum of (JT or pseudo-JT) distorted potential energy surfaces ²

- Break-down of the **Born-Oppenheimer** approximation
- CIs are crucial for signaling the ultrafast decay of excited molecular states
- Nonadiabatic situation



Schematic PES

¹ H. A. Jahn, E. Teller, and F. G. Donnan, Proc. Roy. Soc. A **161**, 220 (1937).

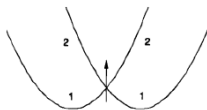
² I.B. Bersuker, The Jahn-Teller effect, Springer series in Chem. Phys. 2009.

The Jahn-Teller theorem

Types of degeneracies

- 1 Conical intersections : JT, PJT & accidental degeneracies
- 2 Glancing interactions : RT

Conical intersections



Glancing interactions



- Group theory : Symmetry selection rule: $[\Gamma_{el}^2] \supset \Gamma_{vib}$

- Three representative cases :

Linear molecules	$[E_k^2] = \sigma + \delta$	no JTE
Tetragonal point groups	$[E^2] = a_1 + b_1 + b_2$	$E \otimes b$ JTE
Trigonal point groups	$[E^2] = a_1 + e$	$E \otimes e$ JTE

Motivation:

- C_3H_4 : Allene (H_2CCCH_2 , D_{2d}), Propyne (H_3CCCH , C_{3v}), and Cyclopropene (C_{2v}) are three stable isomers.
- Allene and Propyne are important intermediates in combustion and astrochemistry, and they are cumulene series with odd number of carbon atoms.
- Allene: $E \otimes b$ JTE and $(E \otimes b) + E$ PJTE
- Propyne: $E \otimes e$ JTE and $(E \otimes e) + A_1$ PJTE

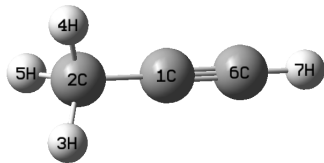
Objectives of our work

- A detailed investigation of multi-mode JT and PJT effects in the first three, $\tilde{X}(^2E)$, $\tilde{A}(^2E)$, and $\tilde{B}(^2A_1)$ electronic states of H_3CCCH^+
- Construct the vibronic model Hamiltonian using the standard vibronic coupling theory
- Extensive *ab initio* quantum chemistry calculations
- JT, PJT and spin-orbit coupling effects in the nuclear dynamics

Electronic structure:

- Symmetry point group : C_{3v}
- Opt/Freq : MP2/aug-cc-pVDZ, G09
- $\Gamma_{vib} = 5a_1 + 5e$
- The symmetrized direct product of E representations in the C_{3v} point group yields

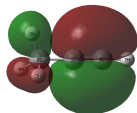
$$\begin{aligned}(E)^2 &= a_1 + e \\ E \otimes A_1 &= e\end{aligned}$$



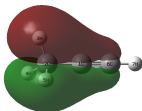
Propyne equilibrium geometry

- The orbital configuration of propyne (H_3CCCH) in its electronic ground state is

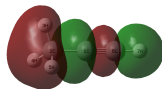
$$\tilde{X}(^1A_1) = (\text{core})(6a_1)^2(7a_1)^2(1e)^4(2e)^4$$



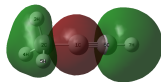
(a) HOMO(2e)



(b) HOMO-1(1e)



(c) HOMO-2(7a₁)



(d) HOMO-3(6a₁)

- Electronic configuration of first three low-lying electronic states of H_3CCCH^+ is

$$\tilde{X}(^2E) = \dots(6a_1)^2(7a_1)^2(1e)^4(2e)^3$$

$$\tilde{A}(^2E) = \dots(6a_1)^2(7a_1)^2(1e)^3(2e)^4$$

$$\tilde{B}(^2A_1) = \dots(6a_1)^2(7a_1)^1(1e)^4(2e)^4$$

Vertical ionization energies

States	$\tilde{X}(^2E)$	$\tilde{A}(^2E)$	$\tilde{B}(^2A_1)$	$\tilde{C}(^2A_1)$	
VIEs	10.23	15.03	15.30	17.78	OVGF
	10.40	15.09	15.31	17.68	EOMIP-CCSD
	10.28	15.40	15.75	18.29	CASSCF-MRC
	10.37	14.70	15.50/15.80	17.49	Expt. ¹
	10.37	14.4	15.13	17.2	Expt. ²
	10.37	14.6	15.3/15.5	17.4	Expt. ³
	10.37	13.69	15.2	17.2	Expt. ⁴
	10.36	13.69/14.70/15.30	15.8	17.49	Expt. ⁵

¹ M. H. Palmer, C. C. Ballard, and I. C. Walker, *Chem. Phys.* **249**, 129 (1999).

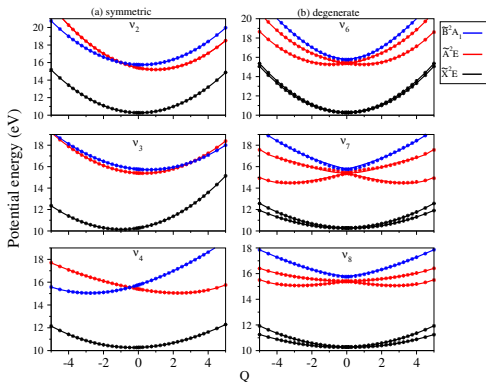
² C. Baker and D. W. Turner, *Proc. R. Soc. London. Ser. A* **308**, 19 (1968).

³ W. Ensslin, H. Bock, and G. Becker, *J. Am. Chem. Soc.* **96**, 2757 (1974).

⁴ D. Frost, F. Herring, C. McDowell, and I. Stenhouse, *Chem. Phys. Lett.* **4**, 533 (1970).

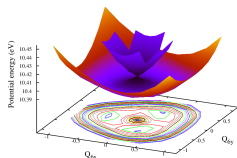
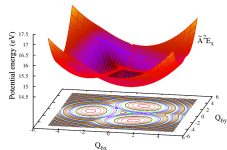
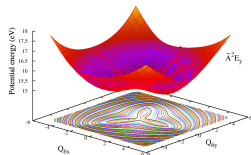
⁵ G. H. Ho, M. S. Lin, Y. L. Wang, and T. W. Chang, *J. Chem. Phys.* **109**, 5868 (1998).

Potential energy surfaces



- $E_{JT}(\tilde{X}^2E) = 0.02 \text{ eV}$ ($\sim 160 \text{ cm}^{-1}$) and Expt.^a, $\sim 117 \text{ cm}^{-1}$
- $E_{JT}(\tilde{A}^2E) = 1.14 \text{ eV}$ ($\sim 11,372 \text{ cm}^{-1}$)
- Spin-orbit (SO) coupling of the \tilde{X}^2E state $\sim -28.60 \text{ cm}^{-1}$ (EOMIP-CCSD) and $\sim -28.83 \text{ cm}^{-1}$ (CASSCF-MRCI), and Marquez *et al.*^a reported $\sim -28 \text{ cm}^{-1}$

^a D. R. Yarkony *et al.*, *J. Phys. Chem. A* **117**, 12002 (2013).



Vibronic coupling model Hamiltonian

$$\mathcal{H} = (\mathcal{T}_N + \mathcal{V}_0)\mathbf{1}_5 + \Delta\mathcal{H}$$

$$\mathcal{T}_N = -\frac{1}{2} \sum_{i \in a_1} \omega_i \frac{\partial^2}{\partial Q_i^2} - \frac{1}{2} \sum_{i \in e} \omega_i \left(\frac{\partial^2}{\partial Q_{ix}^2} + \frac{\partial^2}{\partial Q_{iy}^2} \right),$$

$$\mathcal{V}_0 = \frac{1}{2} \sum_{i \in a_1} \omega_i Q_i^2 + \frac{1}{2} \sum_{i \in e} \omega_i (Q_{ix}^2 + Q_{iy}^2),$$

$$\Delta\mathcal{H} = \begin{pmatrix} u_X^x & u_X^{xy} & 0 & 0 & 0 \\ u_X^{xy} & u_X^x & 0 & 0 & 0 \\ u_A^x & u_A^{xy} & \sum_{i \in e} \lambda'_i Q_{ix} & & \\ h.c. & u_A^y & \sum_{i \in e} -\lambda'_i Q_{iy} & & \\ & & & & u_B^- \end{pmatrix}.$$

diagonal:

$$\begin{aligned} u_j^{x/y} = & E_j^0 + \sum_{i \in a_1} \kappa_i^j Q_i + \frac{1}{2!} \sum_{i \in a_1} \gamma_i^j Q_i^2 + \frac{1}{3!} \sum_{i \in a_1} \sigma_i^j Q_i^3 + \frac{1}{4!} \sum_{i \in a_1} \delta_i^j Q_i^4 \\ & + \frac{1}{2!} \sum_{i \in e} \gamma_i^j (Q_{ix}^2 + Q_{iy}^2) + \frac{1}{3!} \sum_{i \in e} \sigma_i^j (2Q_{ix}^3 - 6Q_{ix}Q_{iy}^2) + \frac{1}{4!} \sum_{i \in e} \delta_i^j (Q_{ix}^4 + 2Q_{ix}^2Q_{iy}^2 + Q_{iy}^4) \\ & + \frac{1}{5!} \sum_{i \in e} \rho_i^j (2Q_{ix}^5 - 4Q_{ix}^3Q_{iy}^2 - 6Q_{ix}Q_{iy}^4) \pm \sum_{i \in e} \lambda_i^j Q_{ix} \pm \frac{1}{2!} \sum_{i \in e} \eta_i^j (Q_{ix}^2 - Q_{iy}^2) \\ & \pm \frac{1}{3!} \sum_{i \in e} \sigma_i'^j (Q_{ix}^3 + Q_{ix}Q_{iy}^2) \pm \frac{1}{4!} \sum_{i \in e} \delta_i'^j (Q_{ix}^4 - 6Q_{ix}^2Q_{iy}^2 + Q_{iy}^4) \pm \frac{1}{4!} \sum_{i \in e} \delta_i''^j (Q_{ix}^4 - Q_{iy}^4) \\ & \pm \frac{1}{5!} \sum_{i \in e} \rho_i'^j (Q_{ix}^5 - 10Q_{ix}^3Q_{iy}^2 + 5Q_{ix}Q_{iy}^4) \pm \frac{1}{5!} \sum_{i \in e} \rho_i''^j (Q_{ix}^5 + 2Q_{ix}^3Q_{iy}^2 + Q_{ix}Q_{iy}^4); j \in \tilde{X}, \tilde{A} \end{aligned}$$

Vibronic coupling model Hamiltonian

$$u_j = E_j^0 + \sum_{i \in a_1} \kappa_i^j Q_i + \frac{1}{2!} \sum_{i \in a_1} \gamma_i^j Q_i^2 + \frac{1}{3!} \sum_{i \in a_1} \sigma_i^j Q_i^3 + \frac{1}{2!} \sum_{i \in e} \gamma_i^j (Q_{ix}^2 + Q_{iy}^2) + \frac{1}{4!} \sum_{i \in e} \delta_i^j (Q_{ix}^4 + 2Q_{ix}^2 Q_{iy}^2 + Q_{iy}^4)$$

off-diagonal:

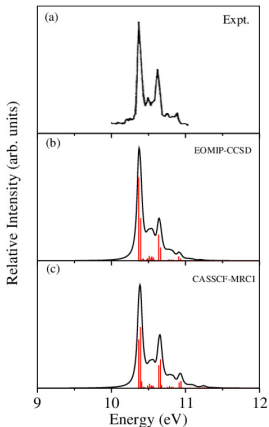
$$\begin{aligned} u_j^{xy} &= \sum_{i \in e} \lambda_i^j Q_{iy} - \frac{1}{2!} \sum_{i \in e} 2\eta_i^j Q_{ix} Q_{iy} + \frac{1}{3!} \sum_{i \in e} \sigma_i^j (Q_{ix}^2 Q_{iy} + Q_{iy}^3) \\ &+ \frac{1}{4!} \sum_{i \in e} \delta_i^j (4Q_{ix}^3 Q_{iy} - 4Q_{ix} Q_{iy}^3) + \frac{1}{4!} \sum_{i \in e} \delta_i^{\prime\prime j} (-2Q_{ix}^3 Q_{iy} - 2Q_{ix} Q_{iy}^3) \\ &+ \frac{1}{5!} \sum_{i \in e} \rho_i^j (-5Q_{ix}^4 Q_{iy} + 10Q_{ix}^2 Q_{iy}^3 - Q_{iy}^5) + \frac{1}{5!} \sum_{i \in e} \rho_i^{\prime\prime j} (Q_{ix}^4 Q_{iy} + 2Q_{ix}^2 Q_{iy}^3 + Q_{iy}^5); j \in \bar{X}, \bar{A} \end{aligned}$$

$$\begin{aligned} u_{AB}^x &= \sum_{i \in e} \lambda_i^{\prime(1)} Q_{ix} + \frac{1}{2!} \sum_{i \in e} \lambda_i^{\prime(2)} (Q_{ix}^2 - Q_{iy}^2) + \frac{1}{3!} \sum_{i \in e} \lambda_i^{\prime(3)} (Q_{ix}^3 + Q_{ix} Q_{iy}^2) \\ &+ \frac{1}{4!} \sum_{i \in e} \lambda_i^{\prime(4)} (Q_{ix}^4 - 6Q_{ix}^2 Q_{iy}^2 + Q_{iy}^4) + \frac{1}{4!} \sum_{i \in e} \lambda_i^{\prime(4')} (Q_{ix}^4 - Q_{iy}^4) \\ &+ \frac{1}{5!} \sum_{i \in e} \lambda_i^{\prime(5)} (Q_{ix}^5 - 10Q_{ix}^3 Q_{iy}^2 + 5Q_{ix} Q_{iy}^4) + \frac{1}{5!} \sum_{i \in e} \lambda_i^{\prime(5')} (Q_{ix}^5 + 2Q_{ix}^3 Q_{iy}^2 + Q_{ix} Q_{iy}^4), \end{aligned}$$

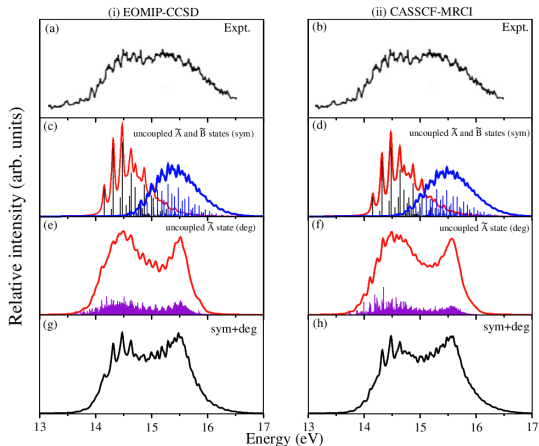
$$\begin{aligned} u_{AB}^y &= \sum_{i \in e} \lambda_i^{\prime(1)} Q_{iy} - \frac{1}{2!} \sum_{i \in e} 2\lambda_i^{\prime(2)} Q_{ix} Q_{iy} + \frac{1}{3!} \sum_{i \in e} \lambda_i^{\prime(3)} (Q_{ix}^2 Q_{iy} + Q_{iy}^3) \\ &+ \frac{1}{4!} \sum_{i \in e} \lambda_i^{\prime(4)} (4Q_{ix}^3 Q_{iy} - 4Q_{ix} Q_{iy}^3) + \frac{1}{4!} \sum_{i \in e} \lambda_i^{\prime(4')} (-2Q_{ix}^3 Q_{iy} - 2Q_{ix} Q_{iy}^3) \\ &+ \frac{1}{5!} \sum_{i \in e} \lambda_i^{\prime(5)} (-5Q_{ix}^4 Q_{iy} + 10Q_{ix}^2 Q_{iy}^3 - Q_{iy}^5) + \frac{1}{5!} \sum_{i \in e} \lambda_i^{\prime(5')} (Q_{ix}^4 Q_{iy} + 2Q_{ix}^2 Q_{iy}^3 + Q_{iy}^5). \end{aligned}$$

Vibrational energy level spectrum:

$\tilde{X}(^2E)$ state



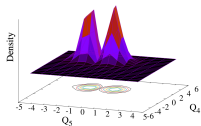
$\tilde{A}(^2E)-\tilde{B}(^2A_1)$ states



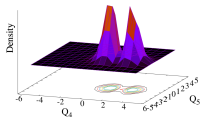
¹C. Baker and D. W. Turner, *Proc. R. Soc. London. Ser. A* **308**, 19 (1968).

Energy eigenvalues (EOMIP-CCSD)

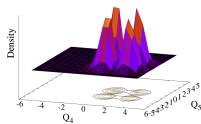
$\tilde{X}({}^2E)$				$\tilde{A}({}^2E)$			$\tilde{B}({}^2A_1)$	
Energy	Ref. [1]	Ref. [2]	Assignment	Energy	Ref. [1]	Assignment	Energy	Assignment
0			0_0^0	0		0_0^0	0	0_0^0
876	940	930 ± 50	$\nu_{5_0}^1$	1024		$\nu_{5_0}^1$	917	$\nu_{5_0}^1$
1328			$\nu_{4_0}^1$	1304	1290	$\nu_{4_0}^1$	1497	$\nu_{4_0}^1$
1752			$\nu_{5_0}^2$	2048		$\nu_{5_0}^2$	1835	$\nu_{5_0}^2$
2169	1940	2000 ± 50	$\nu_{3_0}^1$	2145		$\nu_{3_0}^1$	2018	$\nu_{3_0}^1$
2204			$\nu_{4_0}^1 + \nu_{5_0}^1$	2328		$\nu_{4_0}^2 + \nu_{5_0}^1$	2414	$\nu_{4_0}^1 + \nu_{5_0}^1$
2628			$\nu_{5_0}^3$	2602		$\nu_{4_0}^2$	2752	$\nu_{5_0}^3$
2655			$\nu_{4_0}^2$	3073		$\nu_{5_0}^3$	2936	$\nu_{3_0}^1 + \nu_{5_0}^1$
3046			$\nu_{3_0}^1 + \nu_{5_0}^1$	3169		$\nu_{3_0}^1 + \nu_{5_0}^1$	2991	$\nu_{4_0}^2$
3067			$\nu_{2_0}^1$	3178		$\nu_{2_0}^1$	3017	$\nu_{2_0}^1$
3080			$\nu_{4_0}^1 + \nu_{5_0}^2$	3353		$\nu_{4_0}^1 + \nu_{5_0}^2$	3332	$\nu_{4_0}^1 + \nu_{5_0}^2$



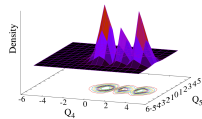
(e) 1024 cm^{-1}



(f) 1304 cm^{-1}



(g) 2328 cm^{-1}



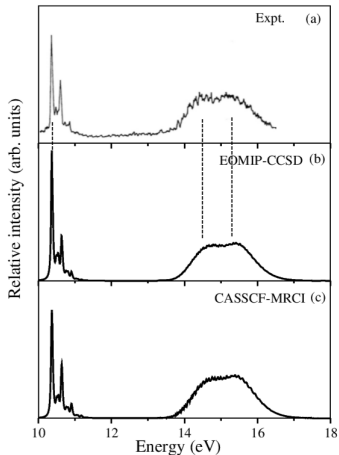
(h) 2602 cm^{-1}

¹ C. Baker and D. W. Turner, *Proc. R. Soc. London. Ser. A* **308**, 19 (1968).

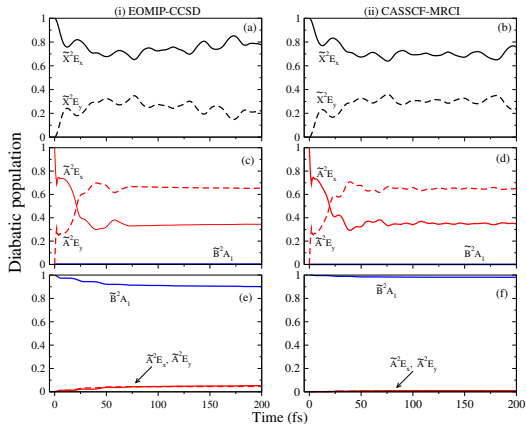
² U. Jacovella and F. Merkt, *Mol. Phys.* **116**, 302 (2018).

Coupled state results

Photoelectron spectrum of propyne



Internal conversion dynamics



¹ C. Baker and D. W. Turner, *Proc. R. Soc. London. Ser. A* **308**, 19 (1968).

Conclusions:

- It is found that the $\tilde{X}(^2E)$ electronic state is energetically well separated from the $\tilde{A}(^2E)$ and $\tilde{B}(^2A_1)$ states at the Franck-Condon geometry.
- Similar results were obtained for the allene radical cation.
- JT effect in the $\tilde{A}(^2E)$ state is stronger than the $\tilde{X}(^2E)$ state.
- The PJT coupling between the $\tilde{A}(^2E)$ - $\tilde{B}(^2A_1)$ electronic states is weak in propyne. But it is stronger in the allene radical cation.
- In case of propyne, the complex band structure of the $\tilde{A}(^2E)$ and $\tilde{B}(^2A_1)$ states arises solely from their energetic proximity.
- This is in contrast to the effects in the vibronic band structure of $\tilde{A}(^2E)$ - $\tilde{B}(^2B_2)$ electronic states of isomeric allene radical cation.

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Thank You