

Suplimentary information

**On the higher-order  $T_2 \otimes (e + t_2)$  Jahn-Teller coupling effects in the photodetachment spectrum of alanate anion  $(\text{AlH}_4^-)^{\text{a}}$**

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The unperturbed nuclear Hamiltonian of the ground electronic state of the  $\text{AlH}_4^-$  anion within a harmonic approximation of nuclear motion is given by  $\mathcal{H}_0 = \mathcal{T}_N + \mathcal{V}_0$ , with

$$\mathcal{T}_N = -\frac{1}{2}\omega_1 \frac{\partial^2}{\partial Q_1^2} - \frac{1}{2}\omega_2 \left( \frac{\partial^2}{\partial Q_{2\theta}^2} + \frac{\partial^2}{\partial Q_{2\epsilon}^2} \right) - \frac{1}{2} \sum_{i \in t_2} \omega_i \left( \frac{\partial^2}{\partial Q_{ix}^2} + \frac{\partial^2}{\partial Q_{iy}^2} + \frac{\partial^2}{\partial Q_{iz}^2} \right),$$

and

$$\mathcal{V}_0 = \frac{1}{2}\omega_1 Q_1^2 + \frac{1}{2}\omega_2 (Q_{2\theta}^2 + Q_{2\epsilon}^2) + \frac{1}{2} \sum_{i \in t_2} \omega_i (Q_{ix}^2 + Q_{iy}^2 + Q_{iz}^2).$$

The quantity  $\omega_i$  represents the harmonic frequency of the vibrational mode  $\nu_i$ . The change of electronic energy upon ionization is expressed by the electronic Hamiltonian matrix  $\mathcal{W}$  in Eq.(1) of the article. The elements of this matrix are expanded in a Taylor series as follows:

$$\begin{aligned} \mathcal{W}_{11} &= E_0 + a_1^{(1)} Q_1 + \frac{1}{2} a_1^{(2)} Q_1^2 + \frac{1}{6} a_1^{(3)} Q_1^3 + \frac{1}{24} a_1^{(4)} Q_1^4 + a_{21}^{(1)} Q_{2\theta} + a_{21}^{(2)} Q_{2\theta}^2 + a_{22}^{(2)} Q_{2\epsilon}^2 + a_{21}^{(3)} Q_{2\theta}^3 \\ &+ a_{22}^{(3)} Q_{2\theta} Q_{2\epsilon}^2 + a_{21}^{(4)} Q_{2\theta}^4 + a_{22}^{(4)} Q_{2\theta}^2 Q_{2\epsilon}^2 + a_{23}^{(4)} Q_{2\epsilon}^4 + \sum_{i \in t_2} \left( a_{i1}^{(2)} Q_{ix}^2 + a_{i2}^{(2)} (Q_{iy}^2 + Q_{iz}^2) + a_{i1}^{(4)} Q_{ix}^4 \right. \\ &\left. + a_{i2}^{(4)} (Q_{iy}^4 + Q_{iz}^4) + a_{i3}^{(4)} Q_{ix}^2 (Q_{iy}^2 + Q_{iz}^2) + a_{i4}^{(4)} Q_{iy}^2 Q_{iz}^2 \right). \\ \mathcal{W}_{22} &= E_0 + a_1^{(1)} Q_1 + \frac{1}{2} a_1^{(2)} Q_1^2 + \frac{1}{6} a_1^{(3)} Q_1^3 + \frac{1}{24} a_1^{(4)} Q_1^4 + a_{21}^{(1)} \left( -\frac{1}{2} Q_{2\theta} + \frac{\sqrt{3}}{2} Q_{2\epsilon} \right) \\ &+ \left( \frac{a_{21}^{(2)}}{4} + \frac{3a_{22}^{(2)}}{4} \right) Q_{2\theta}^2 + \left( \frac{3a_{21}^{(2)}}{4} + \frac{a_2^{(2)}}{4} \right) Q_{2\epsilon}^2 - \left( \frac{\sqrt{3}a_{21}^{(2)}}{2} - \frac{\sqrt{3}a_{22}^{(2)}}{2} \right) Q_{2\theta} Q_{2\epsilon} - \left( \frac{a_{21}^{(3)}}{8} + \frac{3a_{22}^{(3)}}{8} \right) Q_{2\theta}^3 \\ &+ \left( \frac{3\sqrt{3}a_{21}^{(3)}}{8} - \frac{\sqrt{3}a_{22}^{(3)}}{8} \right) Q_{2\epsilon}^3 + \left( \frac{3\sqrt{3}a_{21}^{(3)}}{8} + \frac{\sqrt{3}a_{22}^{(3)}}{8} \right) Q_{2\theta}^2 Q_{2\epsilon} - \left( \frac{9a_{21}^{(3)}}{8} - \frac{5a_{22}^{(3)}}{8} \right) Q_{2\theta} Q_{2\epsilon}^2 \\ &+ \left( \frac{a_{21}^{(4)}}{16} + \frac{3a_{22}^{(4)}}{16} + \frac{9a_{23}^{(4)}}{16} \right) Q_{2\theta}^4 + \left( \frac{9a_{21}^{(4)}}{16} + \frac{3a_{22}^{(4)}}{16} + \frac{a_{23}^{(4)}}{16} \right) Q_{2\epsilon}^4 + \left( -\frac{\sqrt{3}a_{21}^{(4)}}{4} - \frac{\sqrt{3}a_{22}^{(4)}}{4} + \frac{3\sqrt{3}a_{23}^{(4)}}{4} \right) Q_{2\theta}^3 Q_{2\epsilon} \\ &+ \left( \frac{\sqrt{3}a_{21}^{(4)}}{4} + \frac{\sqrt{3}a_{22}^{(4)}}{4} - \frac{3\sqrt{3}a_{23}^{(4)}}{4} \right) Q_{2\theta} Q_{2\epsilon}^3 + \left( \frac{9a_{21}^{(4)}}{8} - \frac{a_{22}^{(4)}}{8} + \frac{9a_{23}^{(4)}}{8} \right) Q_{2\theta}^2 Q_{2\epsilon}^2 \\ &+ \sum_{i \in t_2} \left( a_{i1}^{(2)} Q_{iy}^2 + a_{i2}^{(2)} (Q_{iz}^2 + Q_{ix}^2) + a_{i1}^{(4)} Q_{iy}^4 + a_{i2}^{(4)} (Q_{iz}^4 + Q_{ix}^4) + a_{i3}^{(4)} Q_{iy}^2 (Q_{iz}^2 + Q_{ix}^2) + a_{i4}^{(4)} Q_{iz}^2 Q_{ix}^2 \right). \\ \mathcal{W}_{33} &= E_0 + \sum_{i \in a_1} \left( a_i^{(1)} Q_i + \frac{1}{2} a_i^{(2)} Q_i^2 + \frac{1}{6} a_i^{(3)} Q_i^3 + \frac{1}{24} a_i^{(4)} Q_i^4 \right) + \sum_{i \in e} \left( a_{i1}^{(1)} \left( -\frac{1}{2} Q_{i\theta} - \frac{\sqrt{3}}{2} Q_{i\epsilon} \right) \right. \\ &+ \left( \frac{a_{i1}^{(2)}}{4} + \frac{3a_{i2}^{(2)}}{4} \right) Q_{i\theta}^2 + \left( \frac{3a_{i1}^{(2)}}{4} + \frac{a_{i2}^{(2)}}{4} \right) Q_{i\epsilon}^2 + \left( \frac{\sqrt{3}a_{i1}^{(2)}}{2} - \frac{\sqrt{3}a_{i2}^{(2)}}{2} \right) Q_{i\theta} Q_{i\epsilon} - \left( \frac{a_{i1}^{(3)}}{8} + \frac{3a_{i2}^{(3)}}{8} \right) Q_{i\theta}^3 \\ &- \left( \frac{3\sqrt{3}a_{i1}^{(3)}}{8} - \frac{\sqrt{3}a_{i2}^{(3)}}{8} \right) Q_{i\epsilon}^3 - \left( \frac{3\sqrt{3}a_{i1}^{(3)}}{8} + \frac{\sqrt{3}a_{i2}^{(3)}}{8} \right) Q_{i\theta}^2 Q_{i\epsilon} - \left( \frac{9a_{i1}^{(3)}}{8} - \frac{5a_{i2}^{(3)}}{8} \right) Q_{i\theta} Q_{i\epsilon}^2 \\ &\left. + \left( \frac{a_{i1}^{(4)}}{16} + \frac{3a_{i2}^{(4)}}{16} + \frac{9a_{i3}^{(4)}}{16} \right) Q_{i\theta}^4 + \left( \frac{9a_{i1}^{(4)}}{16} + \frac{3a_{i2}^{(4)}}{16} + \frac{a_{i3}^{(4)}}{16} \right) Q_{i\epsilon}^4 + \left( \frac{\sqrt{3}a_{i1}^{(4)}}{4} + \frac{\sqrt{3}a_{i2}^{(4)}}{4} - \frac{3\sqrt{3}a_{i3}^{(4)}}{4} \right) Q_{i\theta}^3 Q_{i\epsilon} \right) \end{aligned}$$

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$$\begin{aligned}
& + \left( \frac{3\sqrt{3}a_{21}^{(4)}}{4} - \frac{\sqrt{3}a_{22}^{(4)}}{4} - \frac{\sqrt{3}a_{23}^{(4)}}{4} \right) Q_{2\theta} Q_{2\epsilon}^3 + \left( \frac{9a_{21}^{(4)}}{8} - \frac{a_{22}^{(4)}}{8} + \frac{9a_{23}^{(4)}}{8} \right) Q_{2\theta}^2 Q_{2\epsilon}^2 \\
& + \sum_{i \in t_2} \left( a_{i1}^{(2)} Q_{iz}^2 + a_{i2}^{(2)} (Q_{ix}^2 + Q_{iy}^2) + a_{i1}^{(4)} Q_{iz}^4 + a_{i2}^{(4)} (Q_{ix}^4 + Q_{iy}^4) + a_{i3}^{(4)} Q_{iz}^2 (Q_{ix}^2 + Q_{iy}^2) + a_{i4}^{(4)} Q_{ix}^2 Q_{iy}^2 \right). \\
\mathcal{W}_{12} & = \sum_{i \in t_2} \left( b_{i1}^{(1)} Q_{iz} + b_{i1}^{(2)} Q_{ix} Q_{iy} + b_{i1}^{(3)} Q_{iz}^3 + b_{i2}^{(3)} Q_{iz} (Q_{ix}^2 + Q_{iy}^2) + b_{i2}^{(4)} Q_{ix} Q_{iy} (Q_{ix}^2 + Q_{iy}^2) \right) \\
& + \sum_{i \in t_2} b_{2i}^{(2)} \left( -\frac{1}{2} Q_{2\theta} - \frac{\sqrt{3}}{2} Q_{2\epsilon} \right) Q_{iz}. \\
\mathcal{W}_{13} & = \sum_{i \in t_2} \left( b_{i1}^{(1)} Q_{iy} + b_{i1}^{(2)} Q_{iz} Q_{ix} + b_{i1}^{(3)} Q_{iy}^3 + b_{i2}^{(3)} Q_{iy} (Q_{iz}^2 + Q_{ix}^2) + b_{i2}^{(4)} Q_{iz} Q_{ix} (Q_{iz}^2 + Q_{ix}^2) \right) \\
& + \sum_{i \in t_2} b_{2i}^{(2)} \left( -\frac{1}{2} Q_{2\theta} + \frac{\sqrt{3}}{2} Q_{2\epsilon} \right) Q_{iy}. \\
\mathcal{W}_{23} & = \sum_{i \in t_2} \left( b_{i1}^{(1)} Q_{ix} + b_{i1}^{(2)} Q_{iy} Q_{iz} + b_{i1}^{(3)} Q_{ix}^3 + b_{i2}^{(3)} Q_{ix} (Q_{iy}^2 + Q_{iz}^2) + b_{i2}^{(4)} Q_{iy} Q_{iz} \right. \\
& \left. (Q_{iy}^2 + Q_{iz}^2) \right) + \sum_{i \in t_2} b_{2i}^{(2)} Q_{2\theta} Q_{ix}.
\end{aligned}$$

The diagonal elements of the matrix present the diabatic potential energy surfaces of the three components of the  $\tilde{X}^2T_2$  electronic state while the off-diagonal elements are their coupling surfaces. The quantity  $E_0$  is the vertical detachment energy of the ground  $\tilde{X}^2T_2$  electronic state of  $\text{AlH}_4$ . The remaining parameters refer to the coupling constants of different orders, as obtained by the total power of the vibrational coordinate associated with them and is given in the superscript within parenthesis.

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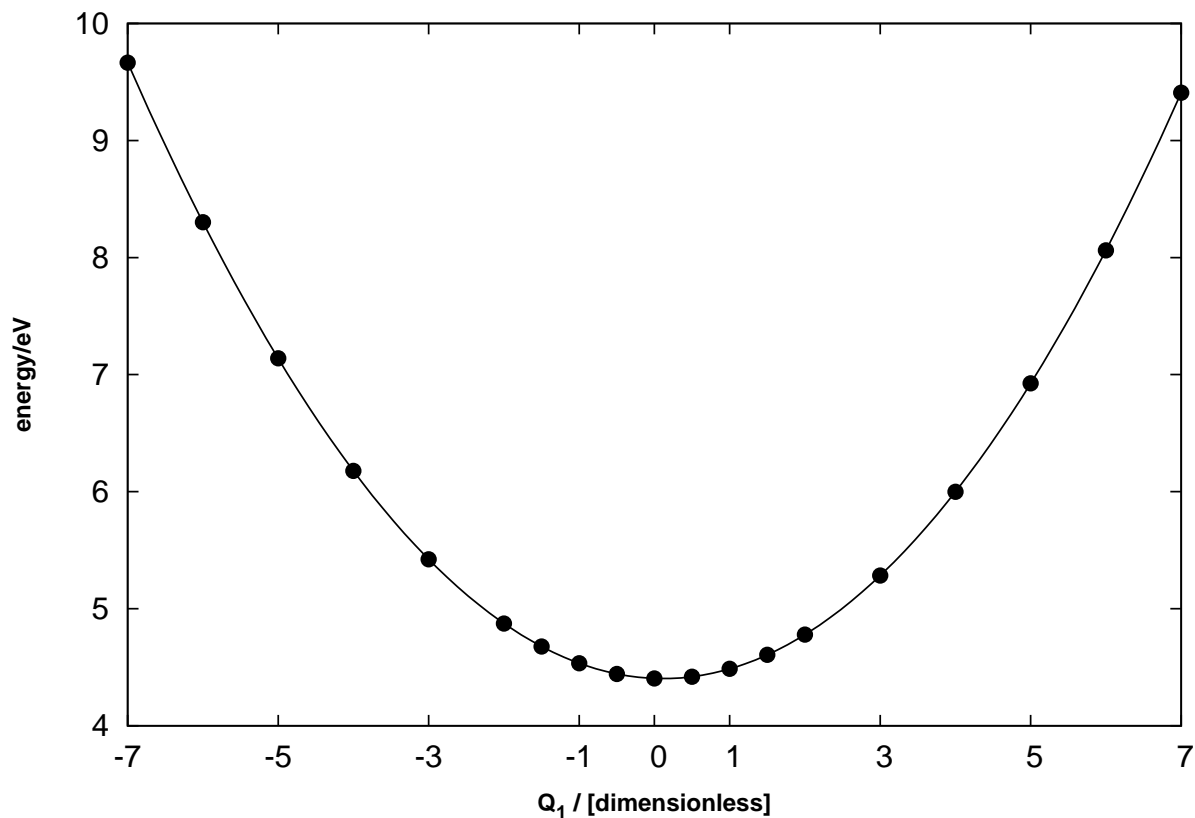


FIG. 1. Adiabatic potentials for the  $\tilde{X}^2T_2$  state of  $\text{AlH}_4$  along the dimensionless normal coordinate of the totally symmetric vibrational mode  $\nu_1$ . The present vibronic model is shown by the solid line and the computed *ab initio* data with a harmonic contribution from the anionic ground electronic state by the solid dots. Energy of the zero point level of the ground electronic state of the anionic  $\text{AlH}_4^-$  at equilibrium configuration ( $Q=0$ ) is set to zero.

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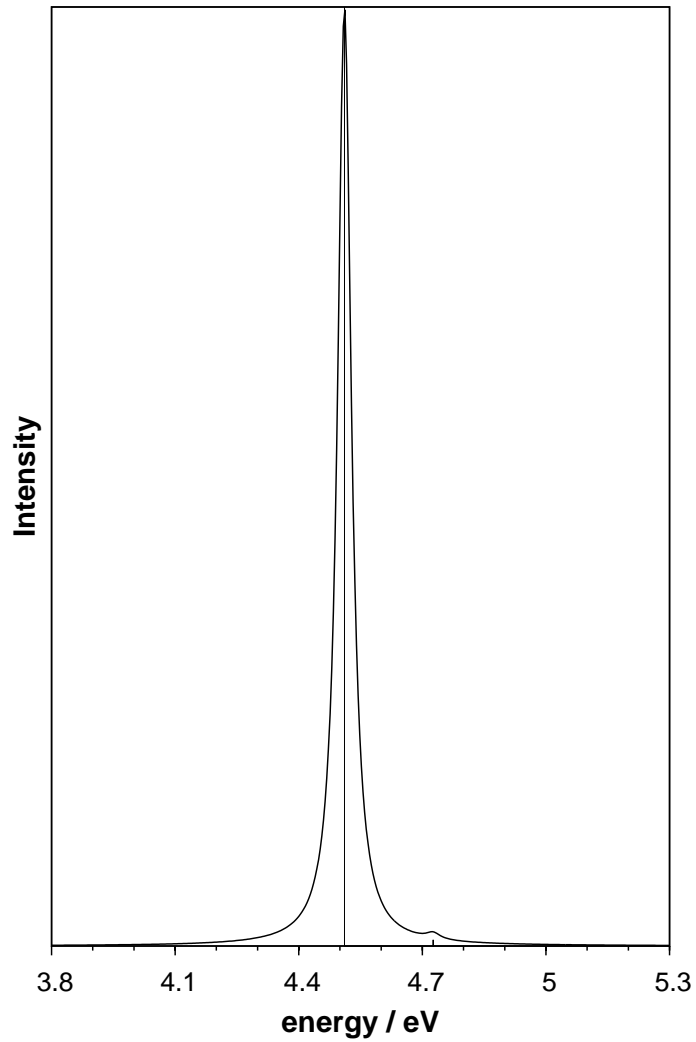


FIG. 2. Partial photodetachment spectrum of the  $\tilde{X}^2T_2$  electronic manifold of  $\text{AlH}_4$  computed with the totally symmetric  $a_1$  vibrational mode  $\nu_1$ . The intensity (in arbitrary units) is plotted as a function of the energy of the final vibronic state. The zero of energy corresponds to the vibrational and electronic ground state  $\text{AlH}_4^-$ . The theoretical stick spectrum is convoluted with a Lorentzian function of 40 FWHM to generate the spectral envelope.