Supplementary notes for "The Jahn-Teller effect in the presence of partial isotopic substitution: the B̃¹E" state of NH₂D and NHD₂"

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These notes amplify the exposition of the Hamiltonian in the main paper.

Degeneracies in the Linear Jahn-Teller Case

The linear Jahn-Teller case specified in equation (15) to (17) in the main paper involves the following terms:

$$\hat{H}_{\text{harm}} = \tfrac{1}{2}\,\omega\!\left(\hat{q}_x^2 + \hat{p}_x^2 + \hat{q}_y^2 + \hat{p}_y^2\right) \tag{1}$$

$$\left\langle \pm \left|\hat{H}_{\text{JT}}\right| \pm \right\rangle = \pm k\omega\hat{q}_x \pm \tfrac{1}{2}\,g\omega\!\left(\hat{q}_x^2 - \hat{q}_y^2\right) \tag{2}$$

$$\left\langle \mathrm{m}\left|\hat{H}_{\text{JT}}\right| \pm \right\rangle = k\omega\hat{q}_y - g\omega\hat{q}_x\hat{q}_y \tag{3}$$

While not immediately obvious, all the eigenvalues of this Hamiltonian are doubly degenerate. This is because the difference in sign between the diagonal linear Jahn-Teller terms is not, in fact significant. If the sign of the wavefunction of levels with n_x odd for the $|-\rangle$ state is changed, then the $\Delta v = \pm 1$ selection rule for $\hat{q}_x$ implies the sign of (the matrix elements of) $\left\langle -\left|\hat{H}_{\text{JT}}\right|-\right\rangle$ is changed but the other linear terms are not. The matrix elements for the $|+\rangle$ and $|-\rangle$ states are then identical and all levels are doubly degenerate if only the linear terms are considered.

This degeneracy is also present when the Hamiltonian is reduced to C_{2v} symmetry, equations (18) to (20) in the main text:

$$\hat{H}_{\text{harm}} = \tfrac{1}{2}\,\omega_x\!\left(\hat{q}_x^2 + \hat{p}_x^2\right) + \tfrac{1}{2}\,\omega_y\!\left(\hat{q}_y^2 + \hat{p}_y^2\right) \tag{4}$$

$$\left\langle \pm \left|\hat{H}_{\text{JT}}\right| \pm \right\rangle = \pm k_x\omega_x\hat{q}_x \tag{5}$$

$$\left\langle \mathrm{m}\left|\hat{H}_{\text{JT}}\right| \pm \right\rangle = k_y\omega_y\hat{q}_y \tag{6}$$

The Hamiltonian matrix splits naturally into two sets (with A_2 and B_1 symmetry for the specific case considered here):

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Overall Symmetry	$\lvert + \rangle$ electronic state	$\lvert - \rangle$ electronic state
A$_2$	$\lvert +, n_x, n_y \rangle$ n_y even	$\lvert -, n_x, n_y \rangle$ n_y odd
B$_1$	$\lvert +, n_x, n_y \rangle$ n_y odd	$\lvert -, n_x, n_y \rangle$ n_y even

Here, n_x and n_y are the number of quanta in the x and y modes. Consideration of the $\hat{H}_{JT}$ operators given above shows that the A$_2$ and B$_1$ matrices are identical, using the same logic as in the D$_{3h}$ case, and so the degeneracy is not lifted.

Energy levels in the purely quadratic Jahn-Teller case

In D$_{3h}$ symmetry the overall symmetry of states with one quantum of a degenerate mode excited is E" × E' = A$_1$" + A$_2$" + E", and three levels are indeed seen. (If only linear terms are included then the A$_1$" and A$_2$" levels remain degenerate). In addition, the selection rules for the q^2 operators of Δv = 0, ±2 means the quadratic terms give rise to effects in first order. For example, the quadratic component of $\hat{H}_{JT}^{(o)} = -g\omega \hat{q}_x \hat{q}_y$ will mix otherwise degenerate components with one quantum of the degenerate mode, giving a Hamiltonian matrix of:

$$
\begin{array}{c|cccc}
 & \lvert +10 \rangle & \lvert -01 \rangle & \lvert +01 \rangle & \lvert -10 \rangle \\
\hline
\langle +10 \rvert & 2\omega + g\omega & -g\omega & & \\
\langle -01 \rvert & -g\omega & 2\omega + g\omega & & \\
\langle +01 \rvert & & & 2\omega - g\omega & -g\omega \\
\langle -10 \rvert & & & -g\omega & 2\omega - g\omega
\end{array}
\tag{7}
$$

where the numbers in the bras and kets are v_x and v_y. This has eigenvalues of $2\omega - g\omega$, 2ω (twice) and $2\omega + g\omega$ as expected from the symmetry argument, and indicating a first order effect giving rise to the splitting (of $g\omega$) between A$_1$" and A$_2$". Symmetry requires that the degeneracy is maintained in the vibrationless level in D$_{3h}$.

Effective Potential

As an alternative to modelling the effects of the Jahn-Teller effect by adding terms to the vibrational Hamiltonian, it is possible to calculate an effective potential energy surface as a function of the vibrational co-ordinates. Considering only the linear terms, this is the eigenvalues of the following matrix:

$$
\begin{pmatrix}
\tfrac{1}{2}\omega\left(q_x^2 + q_y^2\right) + k\omega q_x & k\omega q_y \\
k\omega q_y & \tfrac{1}{2}\omega\left(q_x^2 + q_y^2\right) - k\omega q_x
\end{pmatrix}
\tag{8}
$$

which are:

$$
V\left(q_x, q_y\right) = \tfrac{1}{2}\omega\left(q_x^2 + q_y^2\right) \pm k\omega\sqrt{q_x^2 + q_y^2}
\tag{9}
$$

Recasting in terms of the total displacement from equilibrium, $r = \sqrt{q_x^2 + q_y^2}$ shows that the two dimensional potential only depends on the distance from the origin (at $q_x = q_y = 0$):

$$V(r) = \tfrac{1}{2}\omega r^2 \pm k\omega r \qquad (10)$$

The minimum of this potential is where $\omega r \pm k\omega = 0$, i.e. $r_{min} = \pm k$. This is not a single point, but rather a ring of points or "moat" around the symmetrical point at $r = 0$. The potential at the bottom of the moat is $V(r_{min}) = \tfrac{1}{2}\omega k^2$. Tthe values given in Allen et al[1] imply $\tfrac{1}{2}\omega_3 k_3^2 =$ 45.1 cm^{-1} and $\tfrac{1}{2}\omega_4 k_4^2 = 29.5$ cm^{-1} so it is clear that the maximum in the potential at $r = 0$ is far below the zero point level for both vibrations for the state considered here, so the Jahn-Teller effect is very much a dynamic, rather than a static effect. A similar calculation can be done for the quadratic term, which is known[2] to produce three minima at the bottom of this moat.

Given the force field analysis for NH$_3$ in the main text the above allows a simple static picture of the Jahn-Teller distortion to be developed. The minimum in the effective Jahn-Teller potential occurs at a displacement equal to the Jahn-Teller parameter, k, along the dimensionless normal co-ordinate, q. above. The transformation between these and the internal valence force fields is given as part of the force field analysis, and is shown in Table 1.

Table 1 Transformation matrix, d^{int} between dimensionless normal coordinates and internal coordinates for the B̃^{1}E" state of NH$_3$

	q_1	q_2	q_3		q_4	
δr_1/Å	0.05956	0.00000	0.08631	0.00000	-0.00384	0.00000
δr_2/Å	0.05956	0.00000	-0.04315	0.07474	0.00192	-0.00332
δr_3/Å	0.05956	0.00000	-0.04315	-0.07474	0.00192	0.00332
$\delta\theta_1$/rad	0.00000	0.00000	0.01846	0.00000	0.20361	0.00000
$\delta\theta_2$/rad	0.00000	0.00000	-0.00923	0.01598	-0.10180	0.17633
$\delta\theta_3$/rad	0.00000	0.00000	-0.00923	-0.01598	-0.10180	-0.17633
$\delta\phi$/rad	0.00000	0.30688	0.00000	0.00000	0.00000	0.00000

Given a Jahn-Teller parameter for ν_3 of $k_3 = 0.165$ the above implies the minimum energy geometry corresponds to a displacement of 0.165 along the dimensionless normal coordinate. This does not correspond to a single geometry, but if we just consider one of the components of q_3 and ignore the small mixing between stretching and bending, the table

above allows this to be converted to a geometry where one bond is lengthened by ~0.014 Å and the other two shortened by half that. Similarly the minimum along one of the v_4 modes occurs when one angle is increased by 2.2° and the other two decreased by half that.

Symmetry Coordinates

The transformation between dimensionless normal coordinates and symmetry coordinates is available from the force field analysis:

$$S_1 = 0.103\, q_1 \tag{11}$$

$$S_2 = 0.307\, q_1 \tag{12}$$

$$S_{3x} = 0.106\, q_{3x} - 0.005\, q_{4x} \text{ and } S_{3y} = 0.106\, q_{3y} - 0.005\, q_{4y} \tag{13}$$

$$S_{4x} = 0.023\, q_{3x} - 0.249\, q_{4x} \text{ and } S_{4y} = 0.023\, q_{3y} - 0.249\, q_{4y} \tag{14}$$

The numbers above are in Å or degrees. The conversion factor between S_1 and q_1 in fact has the simple form $\sqrt{h\sqrt{k_{\text{stretch}}m_H}}$ (in SI units) but the others will be more complicated. In particular the mixing between the S_3 and S_4 degenerate modes will depend on the values for k_{stretch} and k_{bend}, though we can see from the figures above that the mixing is small.

Quadratic Jahn-Teller terms in internal coordinates

To see the form of the quadratic Jahn-Teller terms, equation (34) in the main text, in internal co-ordinates expand out the individual terms:

$$
\begin{aligned}
S_{3x}^2 - S_{3y}^2 &= \tfrac{1}{6}\left(4\delta r_1^2 + \delta r_2^2 + \delta r_3^2 - 4\delta r_1\delta r_2 - 4\delta r_1\delta r_3 + 2\delta r_2\delta r_3\right) - \tfrac{1}{2}\left(\delta r_2^2 + \delta r_3^2 - 2\delta r_2\delta r_3\right) \\
&= \tfrac{1}{6}\left(4\delta r_1^2 - 2\delta r_2^2 - 2\delta r_3^2 - 4\delta r_1\delta r_2 - 4\delta r_1\delta r_3 + 8\delta r_2\delta r_3\right)
\end{aligned}
\tag{15}
$$

In terms of internal coordinates this corresponds to a relatively complicated pattern in the force constant matrix:

	δr_1	δr_2	δr_3
δr_1	$4g'$	$-2g'$	$-2g'$
δr_2	$-2g'$	$-2g'$	$4g'$
δr_3	$-2g'$	$4g'$	$-2g'$

(16)

This requires $g' = 2/3\, g_{\text{JT3}}$. The term off-diagonal in electronic state becomes:

$$S_{3x}S_{3y} = \tfrac{1}{2\sqrt{3}}\left(2\delta r_1 - \delta r_2 - \delta r_3\right)\left(\delta r_2 - \delta r_3\right) = \tfrac{1}{2\sqrt{3}}\left(-\delta r_2^2 + \delta r_3^2 + 2\delta r_1\delta r_2 - 2\delta r_1\delta r_3\right) \tag{17}$$

which has a slightly simpler form in internal coordinates:

$$\begin{pmatrix} 0 & g'' & -g'' \\ g'' & -g'' & 0 \\ -g'' & 0 & g'' \end{pmatrix} \qquad (18)$$

where $g'' = -2\sqrt{3}g_{JT3}$.

Fit to determine the Jahn-Teller parameters for the $\tilde{B}^1E''$ state of NH_3

To determine the required parameters a fit was performed to the data shown in Table 2 from Allen et al[4]. Note that the $v_4 > 0$ energies given above came from levels with one quantum of v_2, as a more complete set of observed levels is available, and the data suggests coupling between modes is small.

Table 2 Observed and calculated Vibrational Levels for the $\tilde{B}^1E''$ state of NH_3

	Obs	Obs-Calc
0^0 E''	0.0	−5.7
2^1 E'	898.2	0.0
4^1 E''	1506.0	11.3
4^2 E''	2611.0	6.2
4^2 E''	2776.0	−12.0
$3^1 A_2''$	2770.7	0.1
$3^1 A_1''$	3229.2	0.1
3^1 E''	3401.0	0.0

Normal coordinates for the $\tilde{B}^1E''$ state of NH_2D

It is instructive to look at how the normal coordinates change for NH_2D and ND_2H; see, for example, the transformation between internal and normal coordinates for NH_2D given in Table 3.

Table 3 Transformation between dimensionless normal coordinates and Internal coordinates for the B̃^{1}E" state of NH$_2$D

		q_1	q_2	q_{3x}	q_{3y}	q_{4x}	q_{4y}
		N-H symmetric stretch	umbrella	N-D stretch	N-H asymmetric stretch	HNH bend	HNH wag
δr_1	N-D	-0.01175	0.00000	0.09033	0.00000	-0.00737	0.00000
δr_2	N-H	0.07462	0.00000	0.00736	0.07623	0.00135	-0.00229
δr_3	N-H	0.07462	0.00000	0.00736	-0.07623	0.00135	0.00229
$\delta\theta_1$	H-N-H	-0.01252	0.00000	0.02805	0.00000	0.21828	0.00000
$\delta\theta_2$	H-N-D	0.00626	0.00000	-0.01403	0.01429	-0.10914	0.17394
$\delta\theta_3$	D-N-H	0.00626	0.00000	-0.01403	-0.01429	-0.10914	-0.17394
$\delta\phi$		0.00000	0.29672	0.00000	0.00000	0.00000	0.00000

Note that the degenerate modes separate naturally into N-H and N-D motions. The choice of symmetry coordinates made in the main text means that we can easily correlate modes between the different species.

1. J. M. Allen, M. N. R. Ashfold, R. J. Stickland and C. M. Western, *Mol. Phys.*, 1991, **74**, 49-60.
2. T. A. Barckholtz and T. A. Miller, *Int. Rev. Phys. Chem.*, 1988, **17**, 435-524.