Valence-shell ionization of Acetyl cyanide: simulation of the photoelectron and infra-red spectra: Supporting informations

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I. EXPERIMENTAL SPECTRA

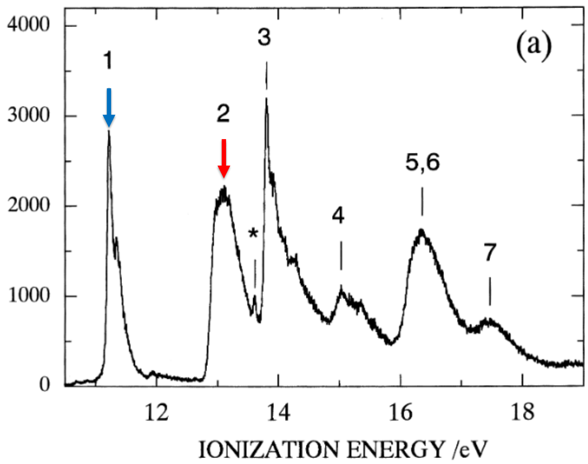

FIG. S1: Experimental photoelectron spectrum of acetyl cyanide taken from Ref.[1]. The blue (red) arrows indicate the two regions of interest corresponding to the 15a'$^{(-1)}$ and 3a"$^{(-1)}$ final states.

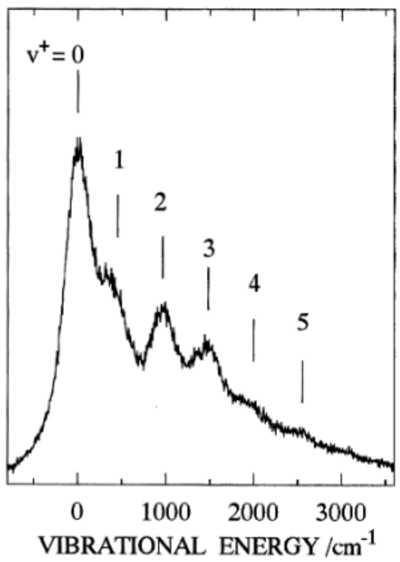

FIG. S2: Recorded photoelectron spectrum of the cationic 15a'$^{(-1)}$ electronic state of acetyl cyanide taken from Ref.[1] showing the vibrational profile extended over 3500 cm^{-1}

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II. THEORETICAL SPECTRA

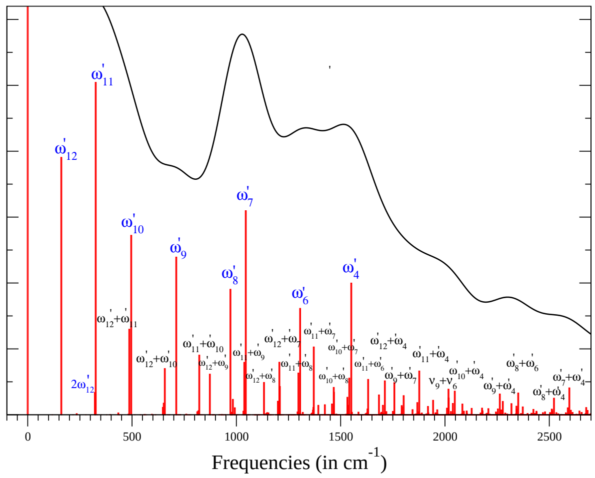

FIG. S3: Assignments of the most important vibrational bands in the satellite energy region (0-2500 cm^{-1}) of the 15a'$^{-1}$ photoelectron line.

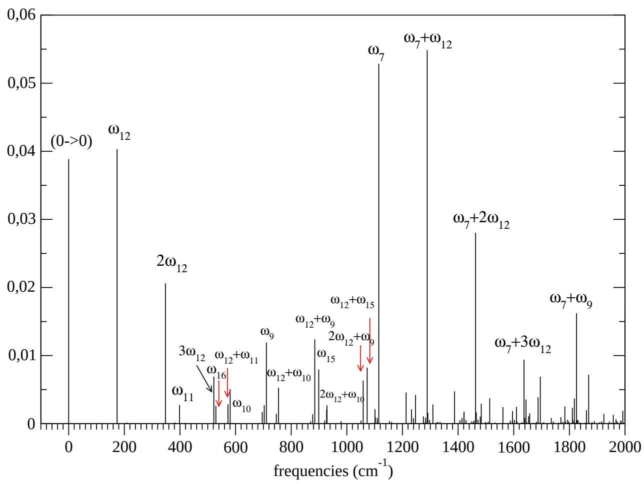

FIG. S4: Assignments of the most important vibrational bands in the satellite energy region (0-2000 cm^{-1}) of the 3a"$^{-1}$ photoelectron line.

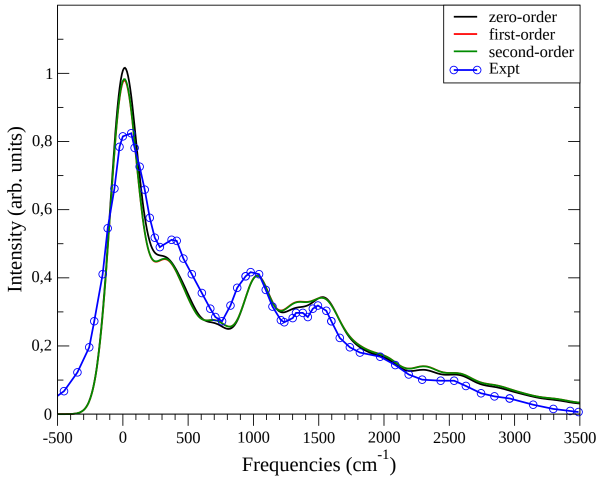

FIG. S5: Simulations at zero-order up to second order (restricted to diagonal terms) approximation of the dipole moment of the 15a'$^{-1}$ photoelectron line. Comparison with experiments is given. The broadening of the bands is fixed to 30 meV.

III. THEORETICAL DETAILS

A. Intensities calculation: Zero-order approximation of the dipole moment

The cross-section σ(v',v) of the vibronic transition between the initial electronic state (denoted o) and the final electronic state (denoted f) is considered to be proportional to the square of the transition dipole matrix element:

$$\sigma(v', v) \propto |\langle\Psi_{v'}^{(f)}|\mu|\Psi_v^{(o)}\rangle|^2 \tag{S1}$$

where $|\Psi_v^{(o)}\rangle$ and $|\Psi_{v'}^{(f)}\rangle$ are the vibronic wave-functions, μ=μ_o+$\sum_{i=1}^{3N-6}[\frac{\partial\mu}{\partial Q_i}]_{Q_i=Q_{i,o}}$ (Q_i-$Q_{o,i}$)+$\frac{1}{2!}$ $\sum_{i=1}^{3N-6}\sum_{j=1}^{3N-6}[\frac{\partial\mu^2}{\partial Q_i \partial Q_j}]$ (Q_i-$Q_{o,i}$)(Q_j-$Q_{o,j}$)+.... is the dipole moment operator, μ_o is the dipole moment of the molecule at the equilibrium geometry, Q_i are the normal modes, $\frac{\partial\mu}{\partial Q_i}$ ($\frac{\partial\mu^2}{\partial Q_i \partial Q_j}$) is the first (second) derivative of the dipole moment with respect to a deformation along the Q_i ($Q_{i,j}$) mode(s) and v(v_1, v_2 . . .)/v'= (v'$_1$, v'$_2$ . . .) are the 3N-6 vibrational modes in the initial (o) and final (f) electronic states. The data have been modeled considering normal modes and frequencies for the initial neutral state and the final cation state, respectively. In first approximation, we assumed that the dipole moment is reduced to its zero order expression, e.g. μ≈μ_o, such that σ(v',v) is restricted to the calculation of the overlap $< \Psi_{v'}^{(f)} l \Psi_v^{(o)} >$ matrix elements.

Let us consider that the vibrational wave function can be express by a product of 3N-6 one-dimensional harmonic oscillator. At the equilibrium geometry (denoted e), the ground state vibrational wave-function is written as a product of 3N-6 independent vibrational wave-functions (N is the number of atoms in the non linear molecule),

$$\Psi_v^{(o)}(\mathbf{R}) = \prod_{k=1}^{3N-6} \chi_{v_k}(Q_k - Q_{o,k}^e; \omega_k) \tag{S2}$$

where $\chi_{v_k}(Q_k - Q_{o,k}^e; \omega_k)$ is a normalized eigenfunction of an harmonic oscillator of reduced mass μ_k centered at $Q_{o,k}^e$ in a vibrational quantum number v_k undergoing vibration along the coordinate Q_k with frequency ω_k.

For the final state, we applied a similar transformation where each lth normal mode of the final state (f) with frequency ω'_l is considered displaced (minimum at $Q'^e_{f,l}$) from the ground state equilibrium position (minimum at $Q^{o}_{f,l}$) and the vibrational wave-function is written as a product of 3N-6 vibrational wave-functions,

$$\Psi^{(f)}_{v'}(\mathbf{R}') = \prod_{l=1}^{3N-6} \chi_{v'_l}(Q'_l - Q'^{e}_{f,l}; \omega'_l) \tag{S3}$$

The vibrational wave-function is expressed as

$$\begin{aligned}\chi_{v'_k}(Q'_l - Q^{e}_{f,k}; \omega'_k) = (2^{v'_k} v'_k!)^{-1/2} (\frac{\beta}{\pi})^{1/4} \\ e^{-\beta\frac{(Q'_l - Q^{e}_{f,k})^2}{2}} H_{v'_k}[\beta^{1/2}(Q'_l - Q^{e}_{f,k})]\end{aligned} \tag{S4}$$

where $H_{v'_k}[\zeta]$ is the Hermite polynomial defined as

$$\begin{aligned}H_{v'_k}[\zeta] &= (-1)^{v'_k} e^{\zeta^2} \frac{d^{v'_k}}{d\zeta^{v'_k}} (e^{-\zeta^2}) \\ &= (-1)^{v'_k} \sum_{j=min}^{v'_k/2} [\gamma_{2j}] \zeta^{2j}\end{aligned} \tag{S5}$$

with $\zeta=\beta^{1/2}(Q'_l - Q^{e}_{f,l})$ ($Q^{e}_{f,l}$ is the equilibrium coordinate for the normal mode k), $\beta = \frac{\mu_k \omega'_k}{\hbar}$, and min=0 or min=$\frac{1}{2}$ according to the parity (even or odd) of v'_k. The components γ_{2j} are given in Table S1.

After some manipulations, a general expression for the overlap between two displaced vibrational states for one normal mode Q_k with occupation numbers $v'_k \geq (v_k = 0)$ can thus be written as

$$\begin{aligned}< \omega'_k, v'_k | \omega_k, 0 >= (-1^{v'_k})(2^{v'_k} v'_k!)^{-1/2} \\ \mu_k^{1/2} \frac{(\omega'_k \omega_k)^{1/4}}{(\hbar\pi)^{1/2}} e^{-[\mu_k \frac{\omega_k \omega'_k}{(\omega'_k + \omega_k)} \frac{(Q^{e}_{f,k} - Q^{e}_{o,k})^2}{2\hbar}]} \\ \sum_{j=min}^{v'_k/2} [\gamma_{2j}] \int_{-\infty}^{\infty} [Q'_k + \frac{\omega_k (Q^{e}_{f,k} - Q^{e}_{o,k})}{(\omega'_k + \omega_k)}]^{2j} \\ e^{-\mu_k \frac{[(\omega'_k + \omega_k) Q'^2_k]}{2\hbar}} dQ'_k\end{aligned} \tag{S6}$$

where in eq.6, $Q'_k = [Q_k - \frac{(\omega'_k Q^{e}_{f,k} + \omega_k Q^{e}_{o,k})}{(\omega'_k + \omega_k)}]$ and $S_k = (RS_k)^2$ ($RS_k = \sqrt{\frac{\mu_k \omega_k}{2\hbar}} (Q^{e}_{f,k} - Q^{e}_{o,k})$) represents the coupling constant associated to the kth normal mode.

For a multi vibrational harmonic model in order to explicitly calculate the coupling constants, we considered here that the change in geometry between the neutral and final states can be described as a vector $\mathbf{\Delta R}$, whose 3N components are the changes in Cartesian

TABLE S1: Analytical Franck-Condon factors FC(ω'_k,v'_k;ω_k,0) between two shifted harmonic PES with fundamental frequencies ω_k and ω'_k, respectively. For α_{2j}, see text.

v_k	v'_k	$[\gamma_{2j}]$					FC	
		γ_0	γ_1	γ_2	γ_3	γ_4	$\omega'_k \neq \omega_k$	$\omega'_k = \omega_k$
0	0	1	0	0	0	0	$2\mathrm{A}\frac{(\omega'_k\omega_k)^{1/2}}{(\omega'_k+\omega_k)}$	e^{-S_k}
0	1	0	-2	0	0	0	$8\mathrm{A}\frac{(\omega'_k\omega_k)^{3/2}}{(\omega'_k+\omega_k)^3}S_k$	$S_k e^{-S_k}$
0	-2	-2	0	4	0	0	$\mathrm{A}\frac{(\omega'_k\omega_k)^{5/2}}{(\omega'_k+\omega_k)^5}[\frac{(\omega'^2_k-\omega^2_k)}{(\omega'_k\omega_k)}+4S_k]^2$	$\frac{S_k^2}{2}e^{-S_k}$
0	3	0	12	0	-8	0	$\frac{4}{3}\mathrm{A}S_k[\frac{(\omega'_k\omega_k)^{7/2}}{(\omega'_k+\omega_k)^7}][3\frac{(\omega'^2_k-\omega^2_k)}{(\omega'_k\omega_k)}+4S_k]^2$	$\frac{S_k^3}{6}e^{-S_k}$
0	4	12	0	-48	0	16	$\frac{3}{4}\mathrm{A}\;\frac{(\omega'_k\omega_k)^{9/2}}{(\omega'_k+\omega_k)^9}[\frac{16}{3}S_k^2+8S_k\frac{(\omega'_k-\omega_k)}{(\omega'_k\omega_k)^2}-\frac{(\omega'^2_k-\omega^2_k)}{(\omega'_k\omega_k)^2}]^2$	$\frac{S_k^4}{24}e^{-S_k}$

A=A(ω'_k,ω_k)= $e^{-2S_k(\frac{\omega'_k}{\omega'_k+\omega_k})}$; $S_k = \mu_k\frac{(Q^e_{f,k}-Q^e_{o,k})^2\omega_k}{2\hbar}$

$Q^e_{f,k}$ and $Q^e_{o,k}$ are the equilibrium cartesian coordinates in the ground and ionized final states, respectively.

coordinates of the atoms in the molecule (see Ref.[2]). We convert this vector to an equivalent vector, $\Delta\mathbf{R}'$ in mass-weighted coordinates by multiplying each component by the square root of the appropriate mass. This, in turn, can be written as a linear combination of the mass-weighted cartesian coordinates $l_{k,j}$ of the vector l_j, where $l_{k,j}=t_{k,j}m_j$,

$$\Delta\mathbf{R}' = \sum_{k=1}^{3N}\Delta Q_k\mathbf{l_k} \tag{S7}$$

for each one-dimensional ΔQ_k term associated to one normal mode k of the initial state, each component $t_{k,j}=\frac{x_{k,j}}{\sqrt{m_j}}$ of kth normal mode delivered by GAMESS(US) package is multiplied by the appropriate atomic mass m_j.

In this case ΔQ_k in length unit can be written as,

$$Q^e_k - Q^o_k = \delta Q_k = \frac{1}{\sqrt{\mu_k}}\sum_{j=1}^{3N}t_{k,j}m_j(X^e_f(j) - X^e_o(j)) \tag{S8}$$

Here, $X^e_f(j) - X^e_o(j)$ is the difference between the jth cartesian coordinates of the ionic state and the neutral ground state and the formula used for S_k is

$$S_k = \frac{\mu_k \omega_k}{2\hbar} \delta Q_k^2 \tag{S9}$$

B. First and second order corrections of the dipole moment

For our purpose, we have reformulated the last term of the general expression ($|<\phi^{\omega'}_{v'_n}|x|\phi^{\omega}_{v_m}>|$) derived by Katriel[3] related to the dipole integrals, where the $|<\phi^{\omega'}_{v'_n}|Q-Q_o|\phi^{\omega}_{v_m}>|$ terms take the final form

$$|<\phi^{\omega'}_{v'_n}|Q-Q_o|\phi^{\omega}_{v_m}>| = \frac{1}{\omega+\omega'}\sqrt{\frac{2\hbar}{\mu}}[\sqrt{n\omega'}I(\omega',n-1,\omega,m)+\sqrt{m\omega}I(\omega',n,\omega,m-1)] + I(\omega',n,\omega,m)\frac{\omega'(Q_e-Q_o)}{\omega+\omega'} \quad \text{(S10)}$$

Here, I(ω',n,ω,m)=$|<\phi^{\omega'}_{v'_n}|\phi^{\omega}_{v_m}>|$ and I(ω',n,ω,m-1) and I(ω',n-1,ω,m) are valid for m$\geq$1 and n$\geq$1, respectively. As a proof, we have fully analytically derived the three expressions, e.g. $|<\phi^{\omega'}_{v'_{n=0,1,2}}|Q-Q_o|\phi^{\omega}_{v_m}>|$ and we have compared them to eq. S10

1. $|<\phi^{\omega'}_{n=0}|Q-Q_o|\phi^{\omega}_{m=0}>|$

First let us write the fundamental (m=n=0) vibrational wave-functions for the initial and final states

$$|\phi^{\omega}_{m=0}>=(\frac{\mu\omega}{\pi\hbar})^{1/4}e^{-\frac{\mu\omega}{2\hbar}}(Q-Q_o)^2 \qquad |\phi^{\omega'}_{n=0}>=(\frac{\mu\omega'}{\pi\hbar})^{1/4}e^{-\frac{\mu\omega'}{2\hbar}}(Q-Q_e)^2 \quad \text{(S11)}$$

The transition matrix element (TME) is given by

$$|<\phi^{\omega'}_{n=0}|(Q-Q_o)|\phi^{\omega}_{m=0}>| = (\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\pi\hbar})^{1/4}\int_{-\infty}^{+\infty} e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}}(Q-Q_o)e^{-\frac{\mu\omega(Q-Q_o)^2}{2\hbar}}dQ \quad \text{(S12)}$$

Let us rearrange the integral part (denoted A) of TME

$$A = e^{-\frac{\alpha\beta(Q_o-Q_e)^2}{\alpha+\beta}}\int_{-\infty}^{+\infty}(Q-Q_o)e^{-(\alpha+\beta)[Q-\frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}]^2}dQ \quad \text{(S13)}$$

where $\alpha=\frac{\mu\omega'}{2\hbar}$ and $\beta=\frac{\mu\omega}{2\hbar}$

By changing variables, e.g. Q→Q'

$$Q' = Q - \frac{(\alpha Q_e + \beta Q_o)}{\alpha + \beta} => Q - Q_o = Q' + \frac{(\alpha Q_e + \beta Q_o)}{\alpha + \beta} - Q_o$$
$$Q - Q_o = Q' + \alpha \frac{(Q_e - Q_o)}{(\alpha + \beta)} \tag{S14}$$

Then, A can be written as

$$A = e^{-\frac{\mu\omega\omega'(Q_o - Q_e)^2}{2\hbar(\omega+\omega')}} (\int_{-\infty}^{+\infty} Q' e^{-(\alpha+\beta)Q'^2} dQ' + [\alpha \frac{(Q_e - Q_o)}{(\alpha + \beta)}] \int_{-\infty}^{+\infty} e^{-(\alpha+\beta)Q'^2} dQ' \tag{S15}$$

The first term of the integral vanishes for parity conditions and A takes the final form

$$A = e^{-\frac{\mu\omega\omega'(Q_o - Q_e)^2}{2\hbar(\omega+\omega')}} [\alpha \frac{(Q_e - Q_o)}{(\alpha + \beta)}] \sqrt{\frac{2\pi\hbar}{\mu(\omega + \omega')}} \tag{S16}$$

Finally TME is given by

$$| < \phi_{n=0}^{\omega'} |(Q - Q_o)| \phi_{m=0}^{\omega} > | = (\frac{\mu\omega}{\pi\hbar})^{1/4} (\frac{\mu\omega'}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega\omega'(Q_o - Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega + \omega')}} [\frac{\omega'(Q_e - Q_o)}{(\omega + \omega')}] \tag{S17}$$

However, the product of the four first terms

$$(\frac{\mu\omega}{\pi\hbar})^{1/4} (\frac{\mu\omega'}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega\omega'(Q_o - Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega + \omega')}} \tag{S18}$$

corresponds to the I(ω',0,ω,0) overlap integral.

Then we can express TME in function I(ω',0,ω,0) to finally obtain

$$| < \phi_{n=0}^{\omega'} |(Q - Q_o)| \phi_{m=0}^{\omega} > | = I(\omega', 0, \omega, 0) \frac{\omega'(Q_e - Q)_o}{\omega + \omega'} \tag{S19}$$

where this expression corresponds to the last term of eq. S10 for which n=m=0.

2. $| < \phi_{n=1}^{\omega'} | Q - Q_o | \phi_{m=0}^{\omega} > |$

Let us write first expressions of the fundamental (m=0,n=1) vibrational wave-functions for the initial and final states

$$|\phi_{m=0}^{\omega} >= (\frac{\mu\omega}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega(Q - Q_o)^2}{2\hbar}} \qquad |\phi_{n=1}^{\omega'} >= \frac{2}{\sqrt{2}} (\frac{\mu\omega'}{\pi\hbar})^{1/4} (\frac{\mu\omega'}{\hbar})^{1/2} (Q - Q_e) e^{-\frac{\mu\omega'(Q - Q_e)^2}{2\hbar}} \tag{S20}$$

The transition matrix element (TME) is written

$$| < \phi_{n=1}^{\omega'} |(Q-Q_o)| \phi_{m=0}^{\omega} > | = \frac{2}{\sqrt{2}} (\frac{\mu\omega'}{\pi\hbar})^{1/4} (\frac{\mu\omega}{\pi\hbar})^{1/4} (\frac{\mu\omega'}{\hbar})^{1/2} \int_{-\infty}^{+\infty} e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}} (Q-Q_o)(Q-Q_e) e^{-\frac{\mu\omega(Q-Q_o)^2}{2\hbar}} dQ \tag{S21}$$

Let us rearrange the integral part (denoted A) of TME

$$A = e^{-\frac{\alpha\beta(Q_o-Q_e)^2}{\alpha+\beta}} \int_{-\infty}^{+\infty} (Q-Q_o)(Q-Q_e) e^{-(\alpha+\beta)[Q-\frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}]^2} dQ \tag{S22}$$

By changing variables, e.g. Q→Q'

$$Q' = Q - \frac{(\alpha Q_e + \beta Q_o)}{\alpha+\beta}$$

$$(Q-Q_e)(Q-Q_o) = Q^2 - Q(Q_e+Q_o) + Q_o Q_e$$

$$=> (Q-Q_e)(Q-Q_o) = [Q' + \frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}]^2 - [Q' + \frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}](Q_e+Q_o) + Q_o Q_e$$

$$Q'^2 + 2Q'\frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta} + [\frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}]^2 - Q'(Q_e+Q_o) - \frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}(Q_e+Q_o) + Q_o Q_e \tag{S23}$$

A can be written as

$$A = e^{-\frac{\alpha\beta(Q_o-Q_e)^2}{\alpha+\beta}} \int_{-\infty}^{+\infty} [Q'^2 + 2Q'\frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta} + [\frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}]^2 - Q'(Q_e+Q_o) - \frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}(Q_e+Q_o) + Q_o Q_e] e^{-(\alpha+\beta)Q'^2} dQ' \tag{S24}$$

after some manipulations, and ignoring Q' odd terms,

$$A = e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}} [\frac{\hbar}{\mu(\omega+\omega')} + (\frac{\omega' Q_e + \omega Q_o}{\omega+\omega'})^2 - (\frac{\omega' Q_e + \omega Q_o}{\omega+\omega'})(Q_e+Q_o) + Q_e Q_o] \tag{S25}$$

Finally the expression of the dipole integral $| < \phi_{n=1}^{\omega'} | Q - Q_o | \phi_{m=0}^{\omega} > |$ is,

$$| < \phi_{n=1}^{\omega'} | Q - Q_o | \phi_{m=0}^{\omega} > | = \frac{2}{\sqrt{2}} (\frac{\mu\omega'}{\pi\hbar})^{1/4} (\frac{\mu\omega}{\pi\hbar})^{1/4} (\frac{\mu\omega'}{\hbar})^{1/2} e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}} [\frac{\hbar}{\mu(\omega+\omega')} + (\frac{\omega' Q_e + \omega Q_o}{\omega+\omega'})^2 - (\frac{\omega' Q_e + \omega Q_o}{\omega+\omega'})(Q_e+Q_o) + Q_e Q_o] \tag{S26}$$

It can be easily shown that

$$(\frac{\omega' Q_e + \omega Q_o}{\omega + \omega'})^2 - (\frac{\omega' Q_e + \omega Q_o}{\omega + \omega'})(Q_e + Q_o) + Q_e Q_o = -\omega\omega'[\frac{(Q_e - Q_o)}{(\omega + \omega')}]^2] \tag{S27}$$

and eq. S26 can be thus reduced to the final form

$$|<\phi^{\omega'}_{n=1}|Q - Q_o|\phi^{\omega}_{m=0}>| = \frac{2}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\hbar})^{1/2} e^{-\frac{\mu\omega\omega'(Q_o - Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega + \omega')}} \\ [\frac{\hbar}{\mu(\omega+\omega')} - \omega\omega'[\frac{(Q_e - Q_o)}{(\omega + \omega')}]^2] \tag{S28}$$

Considering now eq. S10 we have,

$$|<\phi^{\omega'}_{n=1}|Q - Q_o|\phi^{\omega}_{m=0}>| = \frac{1}{\omega + \omega'}\sqrt{\frac{2\hbar}{\mu}}[\sqrt{\omega'} I(\omega', 0, \omega, 0)] + I(\omega', 1, \omega, 0)\frac{\omega'(Q_e - Q_o)}{\omega + \omega'} \tag{S29}$$

Inserting the expression of I(ω',0,ω,0) and I(ω',1,ω,0) into S29

$$I(\omega', 0, \omega, 0) = (\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega\omega'(Q_o - Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega + \omega')}} \\ I(\omega', 1, \omega, 0) = \frac{2}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\hbar})^{1/2} e^{-\frac{\mu\omega\omega'(Q_o - Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega + \omega')}}\omega\frac{(Q_o - Q_e)}{(\omega + \omega')} \tag{S30}$$

we find

$$|<\phi^{\omega'}_{n=1}|Q - Q_o|\phi^{\omega}_{m=0}>| = (\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega\omega'(Q_o - Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega + \omega')}} \\ [\frac{1}{\omega+\omega'}\sqrt{\frac{2\hbar\omega'}{\mu}} - \frac{2}{\sqrt{2}}(\frac{\mu\omega'}{\hbar})^{1/2}\omega\omega'[\frac{(Q_e - Q_o)}{(\omega + \omega')}]^2] \tag{S31}$$

and thus eq. S31 is similar to eq. S28

3. $|<\phi^{\omega'}_{n=0}|Q - Q_o|\phi^{\omega}_{m=1}>|$

Let us write first expressions of the fundamental (m=1,n=0) vibrational wave-functions for the initial and final states

$$|\phi^{\omega'}_{n=0}> = (\frac{\mu\omega'}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega'(Q - Q_o)^2}{2\hbar}} \qquad |\phi^{\omega}_{m=1}> = \frac{2}{\sqrt{2}}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\hbar})^{1/2}(Q - Q_e) e^{-\frac{\mu\omega(Q - Q_e)^2}{2\hbar}} \tag{S32}$$

The fist-order transition matrix element (TME) is written

$$| < \phi^{\omega'}_{n=0}|(Q-Q_o)|\phi^{\omega}_{m=1} > | = \frac{2}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\hbar})^{1/2}\int_{-\infty}^{+\infty} e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}} (Q-Q_o)^2 e^{-\frac{\mu\omega(Q-Q_o)^2}{2\hbar}} dQ \tag{S33}$$

Using the same procedure as we find,

$$| < \phi^{\omega'}_{n=0}|Q-Q_o|\phi^{\omega}_{m=1} > | = \frac{2}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\hbar})^{1/2} e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}}\sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}} [\frac{\hbar}{\mu(\omega+\omega')} + (\frac{\omega' Q_e+\omega Q_o}{\omega+\omega'})^2 - 2(\frac{\omega' Q_e+\omega Q_o}{\omega+\omega'})Q_o + Q_o^2] \tag{S34}$$

where

$$(\frac{\omega' Q_e+\omega Q_o}{\omega+\omega'})^2 - 2(\frac{\omega' Q_e+\omega Q_o}{\omega+\omega'})Q_o + Q_o^2 = \frac{\omega'^2(Q_e-Q_o)^2}{(\omega+\omega')^2} \tag{S35}$$

Then we obtain

$$| < \phi^{\omega'}_{n=0}|Q-Q_o|\phi^{\omega}_{m=1} > | = \frac{2}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\hbar})^{1/2} e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}}\sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}} [\frac{\hbar}{\mu(\omega+\omega')} + \frac{\omega'^2(Q_e-Q_o)^2}{(\omega+\omega')^2}] \tag{S36}$$

After simplifications and introducing the expressions I(ω',0,ω,0) and I(ω',0,ω,1) we find as expected a final expression corresponding to S10.

$$| < \phi^{\omega'}_{n=0}|Q-Q_o|\phi^{\omega}_{m=1} > | = \frac{1}{\omega+\omega'}\sqrt{\frac{2\hbar}{\mu}}[\sqrt{\omega}I(\omega',0,\omega,0)] + I(\omega',0,\omega,1)\frac{\omega'(Q_e-Q_o)}{\omega+\omega'} \tag{S37}$$

where

$$I(\omega',0,\omega,1) = \frac{2}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega}{\hbar})^{1/2} e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}}\sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}} \frac{\omega'(Q_e-Q_o)}{\omega+\omega'} \tag{S38}$$

4. $| < \phi^{\omega'}_{n=2}|Q-Q_o|\phi^{\omega}_{m=0} > |$

Let us write first expressions of the fundamental (m=0,n=2) vibrational wave-functions for the initial and final states

$$|\phi^{\omega}_{m=0} >= (\frac{\mu\omega}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega(Q-Q_o)^2}{2\hbar}} \qquad |\phi^{\omega'}_{n=2} >= \frac{1}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}[-1+\frac{2\mu\omega'}{\hbar}(Q-Q_e)^2]e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}} \tag{S39}$$

The first-order transition matrix element (TME) is written

$$| < \phi^{\omega'}_{n=2}|Q-Q_o|\phi^{\omega}_{m=0} > | = \frac{1}{\sqrt{2}}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}} \sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}}[-\frac{\omega'}{(\omega+\omega')}(Q_e-Q_o)$$
$$+[\frac{2\mu\omega'}{\hbar}][(\frac{3B\hbar}{\mu(\omega+\omega')}+B^3-2B^2Q_e-2\frac{\pi\hbar Q_e}{\mu(\omega+\omega')}+BQ_e^2-(\frac{\hbar Q_o}{\mu(\omega+\omega')}+B^2Q_o^2)+2BQ_oQ_e-Q_oQ_e^2]] \tag{S40}$$

with B$=\frac{\omega' Q_e+\omega Q_o}{(\omega+\omega')}$

5. $| < \phi^{\omega'}_{n=0}|(Q-Q_o)^2|\phi^{\omega}_{m=0} > |$

$$|\phi^{\omega'}_{n=0} >= (\frac{\mu\omega'}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}} \qquad |\phi^{\omega}_{m=0} >= (\frac{\mu\omega}{\pi\hbar})^{1/4} e^{-\frac{\mu\omega(Q-Q_o)^2}{2\hbar}} \tag{S41}$$

$$| < \phi^{\omega'}_{n=0}|(Q-Q_o)^2|\phi^{\omega}_{m=0} > | = (\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\pi\hbar})^{1/4}\int_{-\infty}^{+\infty} e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}}(Q-Q_o)^2 e^{-\frac{\mu\omega(Q-Q_o)^2}{2\hbar}} dQ \tag{S42}$$

Let us write rearrange the integral part (denoted A) of TME

$$A = e^{-\frac{\alpha\beta(Q_o-Q_e)^2}{\alpha+\beta}}\int_{-\infty}^{+\infty}(Q-Q_o)^2 e^{-(\alpha+\beta)[Q-\frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}]^2} dQ \tag{S43}$$

By changing variables

$$Q' = Q - \frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}$$
$$(Q-Q_o)^2 = Q^2 - 2QQ_o + Q_o^2 \tag{S44}$$
$$=> (Q-Q_o)^2 = [Q' + \frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}]^2 - 2[Q' + \frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}] + Q_o^2$$

and introducing eq.S44 into A we obtain the following expression,

$$A = e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}}\sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}}[\frac{\hbar}{\mu(\omega+\omega')}+(\frac{\omega' Q_e+\omega Q_o}{\omega+\omega'})^2-2(\frac{\omega' Q_e+\omega Q_o}{\omega+\omega'})Q_o+Q_o^2] \tag{S45}$$

and finally, using eq.S34, we find that the second-order transition matrix element (TME) takes the final form

$$\begin{aligned}|<\phi^{\omega'}_{n=0}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>| &= (\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\pi\hbar})^{1/4}e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}}\sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}}[\frac{\hbar}{\mu(\omega+\omega')}+(\frac{\omega' Q_e+\omega Q_o}{\omega+\omega'})^2 \\ &\quad -2(\frac{\omega' Q_e+\omega Q_o}{\omega+\omega'})Q_o+Q_o^2] \\ &= \frac{\sqrt{2}}{2}(\frac{\hbar}{\mu\omega})^{1/2}|<\phi^{\omega'}_{n=0}|Q-Q_o|\phi^{\omega}_{m=1}>|\end{aligned} \tag{S46}$$

6. $|<\phi^{\omega'}_{n=1}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>|$

Let us write first expressions of the fundamental (m=0,n=1) vibrational wave-functions for the initial and final states

$$|\phi^{\omega'}_{m=0}> = (\frac{\mu\omega}{\pi\hbar})^{1/4}e^{-\frac{\mu\omega(Q-Q_o)^2}{2\hbar}} \qquad |\phi^{\omega}_{n=1}> = \frac{2}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\hbar})^{1/2}(Q-Q_e)e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}} \tag{S47}$$

The transition matrix element (TME) is written

$$\begin{aligned}|<\phi^{\omega'}_{n=1}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>| = \frac{2}{\sqrt{2}}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\hbar})^{1/2}\int_{-\infty}^{+\infty} e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}} \\ (Q-Q_o)^2(Q-Q_e)e^{-\frac{\mu\omega(Q-Q_o)^2}{2\hbar}}dQ\end{aligned} \tag{S48}$$

Let us rearrange the integral part (denoted A) of TME

$$A = e^{-\frac{\alpha\beta(Q_o-Q_e)^2}{\alpha+\beta}}\int_{-\infty}^{+\infty}(Q-Q_o)^2(Q-Q_e)e^{-(\alpha+\beta)[Q-\frac{(\alpha Q_e+\beta Q_o)}{\alpha+\beta}]^2}dQ \tag{S49}$$

By changing variables

$$
\begin{aligned}
Q' &= Q - \frac{(\alpha Q_e + \beta Q_o)}{\alpha + \beta} \\
(Q - Q_o)^2 &= Q'^2 + 2Q'\frac{(\alpha Q_e + \beta Q_o)}{\alpha + \beta} + [\frac{(\alpha Q_e + \beta Q_o)}{\alpha + \beta}]^2 \\
&\quad -2Q'Q_o - 2\frac{(\alpha Q_e + \beta Q_o)}{\alpha + \beta}Q_o + Q_o^2 \\
(Q - Q_o)^2 &= Q'^2 + 2BQ' + B^2 - 2Q'Q_o - 2BQ_o + Q_o^2 \\
Q - Q_e &= [Q' + \frac{(\alpha Q_e + \beta Q_o)}{\alpha + \beta}] - Q_e = Q' + B - Q_e \\
(Q - Q_e)(Q - Q_o)^2 &= Q'^3 + BQ'^2 - Q_eQ'^2 + 2BQ'^2 + 2Q'B^2 - 2Q'BQ_e \\
&\quad -2Q_oQ'^2 - 2Q'Q_oB + 2Q'Q_oQ_e - 2BQ'Q_o - 2B^2Q_o \\
&\quad +2BQ_oQ_e + Q'Q_o^2 + BQ_o^2 - Q_eQ_o^2 + Q'B^2 + B^3 - Q_eB^2
\end{aligned}
\tag{S50}
$$

Then A can be written as

$$
A = e^{-\frac{\alpha\beta(Q_o - Q_e)^2}{\alpha+\beta}}\sqrt{\frac{2\hbar\pi}{\mu(\omega+\omega')}}[(3B - 2Q_o - Q_e)\frac{\hbar}{\mu(\omega+\omega')} + B^3 - B^2(2Q_o + Q_e) + B(2Q_oQ_e + Q_o^2) - Q_eQ_o^2]
\tag{S51}
$$

and the second-order transition matrix element (TME) takes the expression

$$
|<\phi^{\omega'}_{n=1}|(Q - Q_o)^2|\phi^{\omega}_{m=0}>| = \frac{2}{\sqrt{2}}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\hbar})^{1/2}e^{-\frac{\mu\omega\omega'(Q_o-Q_e)^2}{2\hbar(\omega+\omega')}}\sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}}
[(3B - 2Q_o - Q_e)\frac{\hbar}{\mu(\omega+\omega')} + B^3 - B^2(2Q_o + Q_e) + B(2Q_oQ_e + Q_o^2) - Q_eQ_o^2]
\tag{S52}
$$

with B=$\frac{\omega' Q_e + \omega Q_o}{(\omega+\omega')}$

As in the previous case (see eq.S46), it can be shown (not reported here) that the $|<\phi^{\omega'}_{n=1}|(Q - Q_o)^2|\phi^{\omega}_{m=0}>|$ term can be expressed in function $|<\phi^{\omega'}_{n=1}|(Q - Q_o)|\phi^{\omega}_{m=1}>|$, such as

$$
|<\phi^{\omega'}_{n=1}|(Q - Q_o)^2|\phi^{\omega}_{m=0}>| = \frac{\sqrt{2}}{2}(\frac{\hbar}{\mu\omega})^{1/2}|<\phi^{\omega'}_{n=1}|Q - Q_o|\phi^{\omega}_{m=1}>|
\tag{S53}
$$

7. $|<\phi^{\omega'}_{n=2}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>|$

Let us write again first expressions of the fundamental (m=0,n=2) vibrational wave-functions for the initial and final states

$$|\phi^{\omega'}_{m=0}>=(\frac{\mu\omega'}{\pi\hbar})^{1/4}e^{-\frac{\mu\omega'(Q-Q_o)^2}{2\hbar}} \qquad |\phi^{\omega}_{n=2}>=\frac{1}{\sqrt{2}}(\frac{\mu\omega'}{\pi\hbar})^{1/4}[-1+\frac{2\mu\omega'}{\hbar}(Q-Q_e)^2]e^{-\frac{\mu\omega'(Q-Q_e)^2}{2\hbar}} \tag{S54}$$

After similar transformations, the second-order transition matrix element (TME) takes the final expression

$$\begin{aligned}|<\phi^{\omega'}_{n=2}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>| &= -\frac{1}{\sqrt{2}}|<\phi^{\omega'}_{n=0}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>| \\ &+\frac{1}{\sqrt{2}}(\frac{\mu\omega}{\pi\hbar})^{1/4}(\frac{\mu\omega'}{\pi\hbar})^{1/4}(\frac{2\mu\omega'}{\hbar})e^{-\frac{\mu\omega\omega'(Q_O-Q_e)^2}{2\hbar(\omega+\omega')}}\sqrt{\frac{2\pi\hbar}{\mu(\omega+\omega')}} \\ &[\frac{3\hbar^2}{(\mu(\omega+\omega'))^2}+\frac{6\hbar B^2}{\mu(\omega+\omega')}+B^4-(\frac{6\hbar B}{\mu(\omega+\omega')}+2B^3)(Q_e+Q_o) \\ &+(\frac{\hbar}{\mu(\omega+\omega')}+B^2)(Q_e^2+4Q_eQ_o+Q_o^2)-2B(Q_oQ_e^2+Q_eQ_o^2)+Q_e^2Q_o^2]\end{aligned} \tag{S55}$$

As in the previous case (see eqs. S46 and S53), it can be shown (not reported here) that the $|<\phi^{\omega'}_{n=2}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>|$ term can be expressed in function $|<\phi^{\omega'}_{n=2}|(Q-Q_o)|\phi^{\omega}_{m=1}>|$, such as

The expressions $|<\phi^{\omega'}_{n}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>|$ can be generalized by the using the first-order $|<\phi^{\omega'}_{n}|(Q-Q_o)|\phi^{\omega}_{m=1}>|$ terms.

$$|<\phi^{\omega'}_{n}|(Q-Q_o)^2|\phi^{\omega}_{m=0}>|=|<\phi^{\omega'}_{n}|(Q-Q_o)|\phi^{\omega}_{m=1}>|\frac{\sqrt{2}}{2}\sqrt{\frac{\hbar}{\mu\omega}} \tag{S56}$$

where

$$\begin{aligned}|<\phi^{\omega'}_{n}|(Q-Q_o)|\phi^{\omega}_{m=1}>| &= \frac{1}{\omega+\omega'}\sqrt{\frac{2\hbar}{\mu}}[\sqrt{n\omega'}I(\omega',n-1,\omega,1)+\sqrt{\omega}I(\omega',n,\omega,0)] \\ &+I(\omega',n,\omega,1)\frac{\omega'(Q_e-Q_o)}{\omega+\omega'}\end{aligned} \tag{S57}$$

C. Numerical calculations of the first and second order terms of the dipole moments

The first order derivatives of the dipole moment for each mode ($\frac{\partial\mu}{\partial Q_k}$) was estimated considering small displacements around $Q_{o,k}$, such as $\frac{\partial\mu}{\partial Q_k} \approx \frac{\mu_+ - \mu_-}{Q_{+,k} - Q_{-,k}}$ where

$$Q_{+,k} - Q_{-,k} = \frac{1}{\sqrt{\mu_k}} \sum_{j=1}^{3N} t_{k,j} m_j (x_{+,j} - x_{-,j}) \tag{S58}$$

with the kth new coordinates ($x_{\pm,k}(l,\delta)$) are obtained along a deformation along the $Q_{o,l}$ mode from the equilibrium coordinates ($x_{o,k}$)

$$x_{\pm,k}(l,\delta) = x_{o,k} + \delta . t_{l,k} . \sqrt{\mu_l} . Q_{o,l} \tag{S59}$$

For modes (18,17,15,14,13), δ was set to 1000. For modes (16), δ was set to 100. For the rest modes, δ was set to 0.1.

The second order derivatives of the dipole moment for each mode ($\frac{\partial^2\mu}{\partial Q_k^2}$) was estimated using eq.S10, such as

$$\frac{\partial^2\mu}{\partial Q_k^2} \approx \frac{\mu(Q_o + \delta Q_k) + \mu(Q_o - \delta Q_k) - 2\mu_o}{\Delta Q_k^2} \tag{S60}$$

where $\mu(Q_o \pm \delta Q_k) = \mu(Q_{\pm,k}(\delta))$ and

$$\Delta Q_k = Q_{+,k}(\delta) - Q_{o,k} \tag{S61}$$

μ_o is the dipole moment of the molecule at the equilibrium geometry.

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TABLE S2: Modes(ω_i, i=1,3N-6). Q_i(i=1,3 N-6) normal coordinates (in Å). Frequencies (in cm^{-1}). In parenthesis, order of frequencies by increasing value. Derivatives (in Debye $Å^{-1}$units) and second derivatives (Debye $Å^{-2}$) of the Dipole moment. First-order (in Å(x 10^5)) and second-order (in $Å^2$ (x 10^5)) components of the dipole.

$Mode_i$	$Q_{o,i}$(in Å)	ω_i	$\frac{\partial\mu}{\partial Q_i}$	$< \omega'_i, 0\|Q - Q_{o,i}\|\omega_i, 0 >$ $(^a)$	$< \omega'_i, 1\|Q - Q_{o,i}\|\omega_i, 0 >(^a)$	$< \omega'_i, 2\|Q - Q_{o,i}\|\omega_i, 0 >(^a)$	$\frac{\partial^2\mu}{\partial Q_i^2}$	$\frac{1}{2} < \omega'_i, 0\|(Q - Q_{o,i})^2\|\omega_i, 0 >(^a)$	$\frac{1}{2} < \omega'_i, 1\|(Q - Q_{o,i})^2\|\omega_i, 0 >(^a)$	$\frac{1}{2} < \omega'_i, 2\|(Q - Q_{o,i})^2\|\omega_i, 0 >(^a)$
ω_{18}	-0.0003	129 (1)	0.00	-14	35128	21	0.008	6473	-2	8518
ω_{17}	-0.0001	245 (3)	0.00	1	8852	-1	-0.390	417	0	536
ω_{16}	-0.0022	596 (5)	0.00	3523	7915	-5264	0.724	591	113	495
ω_{15}	0.0001	1049 (9)	0.00	3107	8166	-4188	0.264	504	132	529
ω_{14}	0.0008	1468 (13)	0.00	-3	10473	4	0.836	557	0	769
ω_{13}	0.0003	3086 (17)	0.00	0	7046	0	-0.652	250	0	350
ω_{12}	0.3230	177 (2)	1.16	5381	8517	-7219	0.744	908	-225	652
ω_{11}	-2.2169	437(4)	0.77	-4238	6046	6321	-0.080	592	-78	327
ω_{10}	-1.0770	599 (6)	-0.02	3	5833	-4	0.418	175	0	237
ω_9	-5.0203	715 (7)	-1.22	2546	5671	-3348	1.263	273	76	265
ω_8	-1.9134	985 (8)	1.13	-1	8716	1	0.635	396	0	526
ω_7	-0.0298	1193 (10)	-0.25	2654	5067	-3742	2.272	270	61	215
ω_6	0.2854	1398 (11)	-1.00	2891	8249	-4081	1.355	504	115	525
ω_5	-0.6758	1458 (12)	-0.20	928	10329	-1352	1.110	561	45	751
ω_4	-2.6355	1776 (14)	-0.74	-1011	2295	1461	1.042	47	-10	42
ω_3	-1.2758	2323 (15)	0.94	-243	2347	343	0.358	28	-3	39
ω_2	-1.7862	3031 (16)	-0.14	-235	7308	337	-0.409	270	-8	376
ω_1	-0.3301	3146 (18)	0.22	227	6951	-320	-0.658	242	7	342