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Deduction of Bond Length Changes of Symmetric Molecules from Experimental Vibrational Progressions, Including a Topological Mass Factor[§]

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S *Supporting Information*

ABSTRACT: The change ΔR_x of bond length R_x for atom X in a molecule upon electronic transition can be derived from the intensities I_i of the vibrational stretching progression $v = 0 \rightarrow i$ of the electronic absorption or emission spectrum. In many cases, a simple model is sufficient for a reasonable estimate of ΔR_x. For symmetric molecules, however, conceptual problems in the literature of many decades are evident. The breathing modes of various types of symmetric molecules X_n and AX_n (A at the center) are here discussed. In the simplest case of a harmonic vibration of the same mode in the initial and final electronic states, we obtain $\Delta R_x \approx [2S/(\omega m_x)]^{1/2}/\underline{w}^{1/2}$ (all quantities in atomic units). ω and S are respectively the observed vibrational quanta and the Huang–Rhys factor (corresponding, e.g., to the vibrational intensity ratio $I_1/I_0 \approx S$), m_x is the mass of vibrating atom X, and $\underline{w}$ is a topological factor for molecule X_n or AX_n. The factor $1/\underline{w}^{1/2}$ in the expression for ΔR_x must not be neglected. The spectra and bond length changes of several symmetric molecules AX_n and X_n are discussed. The experimental bond length changes correctly derived with factor $1/\underline{w}^{1/2}$ are verified by reliable quantum chemical calculations.

$\Delta R_x \sim \sqrt{2S/(\underline{w} \cdot m_x \omega)}$

$S \approx 1.0, \underline{w} = 2$ for X–A–X
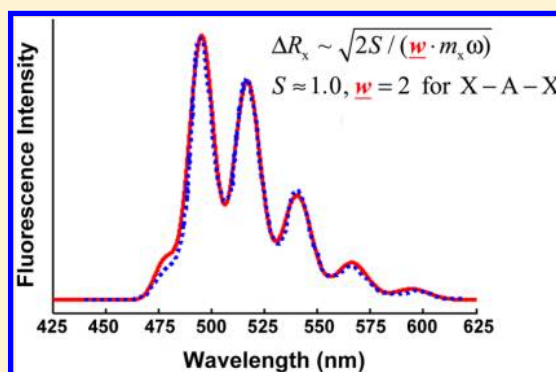
INTRODUCTION

Many electronic excitation and deexcitation processes of molecules upon absorption and emission of light are related to one-electron jumps between one of the energetically higher occupied molecular orbitals (HOMOs) and one of the virtual lower unoccupied molecular orbitals (LUMOs). Often, the bonding characters of the two, mainly involved molecular orbitals (MOs) are different, such as bonding HOMO and antibonding or nonbonding LUMO, or the electronic jump corresponds to an interatomic charge transfer changing the ionic interaction between the atoms. Then the internuclear distances and angles will change upon the electronic jump, which induces changes of the nuclear vibrations. Accordingly, the electronic excitation, ionization, and de-excitation spectra appear in the form of vibrational progressions.

In principle, the electronically induced change of length, ΔR_x, of a bond to atom X with mass m_x, can easily be estimated from the observed intensity pattern (as characterized by Huang–Rhys factor S) of the vibrational bond stretching progression with frequency ω_f of the electronic final state. However, some literature data from the last five decades up to present times exhibit inconsistencies, due to some conceptual mix-up. Namely, the formula for the most simple case of a single atom, vibrating against a fixed point, I←X, reads $\Delta R_x \approx [2S/(\omega_f m_x)]^{1/2}$ (in atomic units). For symmetric polyatomic molecules X_n or AX_n, $n \geq 2$,

the same formula has often been applied (see ref 1 and further references below). It has been argued that the central point of a symmetric molecule does not move in the case of the totally symmetric breathing mode, and that the vibrations of molecule AX_n are therefore equivalent to those of I–X, with m_x being the effective vibrating mass, $m_{eff} = m_x$. When the resulting prediction of ΔR_x is the only available one, an incorrectly determined ΔR_x is not easily recognized. Nowadays, however, ΔR_x values of electronically excited states can also be determined reliably by quantum chemical calculations. This motivated us to upgrade the formula for ΔR_x by a correcting topological atomic weight factor $1/\underline{w}^{1/2}$ for molecules X_n and AX_n, where the atomic mass m_x must be replaced by an effective mass $m_{eff} = \underline{w}m_x$.

The proper $\underline{w}$-factors will be derived in the Theory. They will be corroborated in the Experimental Examples by comparing quantum chemical calculations of initial and final electronic molecular states with experimental spectra (such as UV–vis absorption or emission spectra; electron energy loss, e–2e, photoelectron and electron detachment spectra). The molecular examples comprise "old and famous" ones (N_2, MnO_4^-, P_4) as well as more "topical" ones (actinide molecules UO_2^{2+}, $(UO_2)F_4^{2-}$, UF_6, and TcO_4^-).

If not stated otherwise, atomic units (au) are used: Planck's reduced constant $\hbar = h/2\pi = 1$ au; electronic charge e $= -1$ au; electronic mass $m_e = 1$ au (i.e., chemical mass unit $u(^{12}C/12) = 1822.888$ au); dielectric vacuum constant $4\pi\varepsilon_0 = 1$ au (i.e., vacuum velocity of light $c = 1/\alpha$ au, with Sommerfeld's constant $\alpha = 137.036$; energy unit of 1 au $= 27.2114$ eV, corresponding to 219 475 cm^{-1}; length unit of 1 au $= 52.9177$ pm). Often we will simply omit the "au".

2. THEORY

We discuss symmetric vibrations of symmetric molecules AX_n, where A may be a real atom—different from or equal to X (i.e., X_{n+1})—or just the virtual central point (i.e., molecule X_n). We think of linear diagonal molecules AX_2 or X_2 of $D_{\infty h}$ symmetry (e.g., $[UO_2]^{2+}$ or N_2); of planar trigonal molecules AX_3 or X_3 of D_{3h} type (e.g., NO_3^- or $(CH_2)_3$); of planar tetragonal or three-dimensional tetrahedral molecules AX_4 or X_4 of D_{4h} or T_d type (e.g., $[(UO_2)F_4]^{2-}$, $[MnO_4]^-$, $[TcO_4]^-$, P_4); of octahedral molecules AX_6 or X_6 of O_h type (e.g., UF_6, $Cr(CO)_6$); of dodeca/icosahedral molecules AX_{12} or X_{12} of I_h type (e.g., WAu_{12});[2,3] and so on. We will here not discuss how to marginally improve on the fitting of experimental spectra by a better model (for instance accounting for anharmonicities). Our point is the large change of the *physical* bond length parameter, when it is *correctly* deduced from the same model and model parameters as applied and derived by various spectroscopists.

The relation between the bond length change and the Huang−Rhys factor of a single atom vibrating against a fixed point was given above. In the totally symmetric stretching mode of a symmetric molecule AX_n or X_n, the central atom or point does not move. However, it is impossible for a single atom X_i in a polyatomic molecule to vibrate without vibration of the other, symmetry equivalent atoms. This changes the effective mass and causes a factor $1/\underline{w}^{1/2}$ in the expression for ΔR_x. To make the point clear, we will here assume the harmonic approximation without Jahn−Teller distortions or Duschinsky rotations, i.e., similar vibrational modes in the initial (i) and final (f) electronic states with frequencies $\omega = \omega_i = \omega_f$. Corrections equivalent to the factor $1/\underline{w}^{1/2}$ derived below can then be easily introduced into the formulas of more complex and more realistic cases (with $\omega_i \neq \omega_f$ and with anharmonicity) as treated by Hutchisson,[4,5] Fonger and Struck,[6,7] Denning,[8] and others.[9−12]

2.1. Harmonic Model without Change of Mode upon Electronic Excitation. Comprehensive formulas for the intensities of vibrational transitions in the harmonic Born−Oppenheimer Franck−Condon approximation were given by Fonger and Struck.[6,7] We simplify their formulas to the case of a common vibrational normal mode, i.e., with same reduced mass μ, force constant k, vibrational quanta $\hbar\omega = (k/\mu)^{1/2}$, and normal coordinates Q for initial and final electronic states. For a change ΔR_x of equilibrium internuclear distance from the initial to the final electronic state, the Huang−Rhys factor S is here defined as

$$S = \frac{k_f}{2}\Delta R_x{}^2/\omega_f \tag{1}$$

which is the energy increase on the potential energy surface of the final electronic state from its minimum to the value at vertical electronic transition, in units of the vibrational quantum of the final electronic state. The relative intensities I_{0v} of the progression of vibrational bands $0 \rightarrow v$ (Figure 1) are then given in terms of the Huang−Rhys factor S by
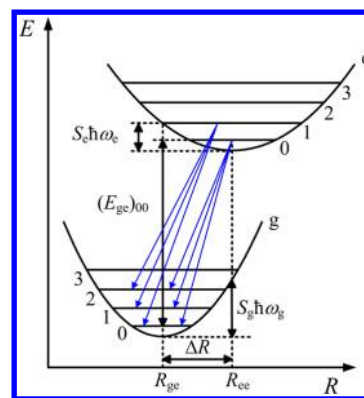

Figure 1. Energy E versus bond length R_x of the electronic ground (g) and excited (e) states. R_{ge} and R_{ee} are the respective equilibrium values, $\Delta R_x = |R_{ge} - R_{ee}|$ is the change upon electronic excitation. $(E_{ge})_{00}$ is the adiabatic electronic excitation energy between the vibrational 0-levels, $S\hbar\omega$ represents the adiabatic-vertical energy level differences for excitation and deexcitation, and S_g and S_e are the respective Huang−Rhys factors. Progression e0 $\rightarrow$ g0,1,2 and hot bands e1 $\rightarrow$ g0,1,2 are indicated by arrows.

$$\frac{I_{0v}}{I_{00}} = \frac{S^v}{v!}(1 + \kappa) \tag{2}$$

The absorption and emission intensities are, respectively, proportional to the first and third powers of the transition energies $E_{if} = E_{00} \pm v\hbar\omega_f$, which are here approximated by the first two terms of a binomial expansion, $E^n = (E_{00} + \Delta)^n \approx E_{00}{}^n[1 + n(\Delta/E_{00})]$. That is, $\kappa = +vr$ for absorption and $\kappa = -3vr$ for emission, where $r = \omega_f/E_{00}$, with adiabatic excitation energy E_{00}. At the qualitative level, and for large E_{00} and small ω_f, r may be neglected. The intensity ratios $(\omega_i = \omega_f)$ for the first three vibration bands are then simply approximated by

$$I_{00}{:}I_{01}{:}I_{02}{:}I_{03} = 1{:}[S]{:}[S^2/2]{:}[S^3/6] \tag{3}$$

This gives a first impression and rule of thumb for the magnitude of S in the case of an experimentally resolved vibrational progression. For more accurate determinations, numerical computations accounting for anharmonicity, for $\omega_i \neq \omega_f$, for Dushinsky rotation and for vibrational couplings are required, of course. In the case of unresolved progressions, one may approximately identify the intensity maximum with E_{vert} and determine the (fractional) v_{max} value from

$$v_{max} = |E_{vert} - E_{00}|/\omega_f \tag{4}$$

v_{max} is related to the Huang−Rhys factor S by (see also the Supporting Information)

$$S \approx v_{max}(1 - \kappa') + \frac{1}{2} \tag{5}$$

where $\kappa' = +r$ for absorption or $-3r$ for emission. We stress that eq 5 turned out to be rather accurate even for small S values.

To clarify the problem with symmetric vibrations of symmetric molecules, we will discuss such cases explicitly. The results are well-known in principle, though often not considered in practice.

2.2. Single Bond Case I−X. We discuss the Franck−Condon ratios of the first few bands of the stretching progression for an atom X vibrating against a virtual fixed point. Let the force constant be k_x and the vibrating mass be m_x. The equilibrium values R_e of coordinate R_x in the electronic initial and final states are defined, respectively, as $R_{ie} = 0$ and $R_{fe} = \Delta R_x$.

The Schrödinger equation in terms of variable R_x and with vibrational quantum $\hbar\omega = (k_x/m_x)^{1/2}$ (equal to the angular frequency ω, if au are used) reads

$$\left\{-\frac{1}{2m_x}\frac{\mathrm{d}^2}{\mathrm{d}R_x^{\,2}} + \frac{k_x}{2}(R_x - R_e)^2 - \left(v + \frac{1}{2}\right)\sqrt{\frac{k_x}{m_x}}\right\}\Psi_v(R_x)$$
$$= 0 \qquad (6)$$

The lowest solutions given in the Supporting Information file yield the Franck–Condon intensity ratios, eq 3, in terms of ΔR_x, related to the Huang–Rhys factor by

$$\Delta R_x = \sqrt{2S/(\omega_f m_x)} = \sqrt[4]{4S^2/(k_x m_x)} \qquad (7)$$

(where we have neglected for simplicity the energy factors for absorption or emission).

In passing, we also present the relative intensities of the first three hot bands from thermally populated vibration level $v = 1$ at temperature T, in terms of the Huang–Rhys factor S and the Boltzmann factor $B = e^{-k_B T/\hbar\omega}$ ($k_B = 3.1668 \times 10^{-6}$ au/K $\sim 0.695\,04$ cm^{-1}/K):

$$I_{00}{:}I_{10}{:}I_{11}{:}I_{12} = 1{:}[BS]{:}[B(1-S)^2]{:}[BS(2-S)^2/2] \qquad (8)$$

From the observed progression intensities, eqs 3 or 4 or 8, one obtains S, and then the approximate bond length change by eq 7. This rule of thumb can then be used for a first estimate of ΔR and then for cross-checking the value derived from more accurate explicit numerical computations.

2.3. General Case AX$_n$. We assume the same A–X force constant k_x and the same change ΔR_x of A–X bond length R_x as before. The transformation to normal coordinates yields a decoupled Schrödinger equation for the breathing mode which reads, for the final state:

$$\left\{-\frac{1}{2m_{\mathrm{eff}}}\frac{\mathrm{d}^2}{\mathrm{d}R_x^{\,2}} + \frac{k_{\mathrm{eff}}}{2}(R_x - R_{fe})^2 - \left(v + \frac{1}{2}\right)\sqrt{\frac{k_{\mathrm{eff}}}{m_{\mathrm{eff}}}}\right\}\Psi_v(R_x) = 0 \qquad (9)$$

Equation 9 is in terms of variable R_x, so that we can directly read off the values of $R_{fe} = \Delta R_x$, $k_{\mathrm{eff}} = f k_x$, and $m_{\mathrm{eff}} = \underline{w} m_x$. The factor f for the effective force constant is the number of equivalent bonds with force constant k_x. The factor $\underline{w}$ relates the mass m_x of a single atom to the effective vibrating mass of the molecule. The latter is the number of equivalent vibrating atoms, times a kinematic factor g^2 with $g = $ (change of nuclear position)/(change of bond length). Then we define the normal coordinate for the symmetric stretch as $\Delta Q = (\underline{w} m_x)^{1/2}\Delta R_x$. For centric AX$_n$ molecules with n bonds A–X, $f = n$, and for the atoms X vibrating in the A–X bond direction against an atom A or central point at rest, $\underline{w} = n$. The vibrational quanta for the case of centric molecules AX$_n$, $\omega' = (k_{\mathrm{eff}}/m_{\mathrm{eff}})^{1/2} = (k_x/m_x)^{1/2}$, are the same as in the single bond case, but the formula for the bond length change now reads

$$\Delta R_x = \sqrt{2S/(\omega' m_x)}\sqrt{1/\underline{w}} = \sqrt[4]{4S^2/(k_x m_x)}\sqrt[4]{1/(f\underline{w})} \qquad (10)$$

In terms of common units, ω' in cm^{-1}, m_x in "chemical atomic mass units" u, and ΔR_x in picometers, it reads

$$\Delta R_x = 821\ \mathrm{pm}\ \sqrt{\frac{\underline{w}^{-1}S}{(m_x/[\mathrm{u}])(\omega'_f/[\mathrm{cm}^{-1}])}} \qquad (11)$$

We will now discuss a pair of simple cases, X$_2$ and AX$_2$, which appears somewhat counterintuitive at first naive sight.

2.4. Diatomic Case X–X. We again assume the same force constant k_x and bond length change ΔR_x as before. There are now two vibrating atoms. The transformation from the two Cartesian coordinates x_1, x_2 of the two atoms to the two relative coordinates, center of gravity X_{cg} (molecular midpoint) and bond length R_x (with equilibrium value $R_e = 0$ and $R_e = \Delta R_x$ for the initial and final states), is $x_1 = X_{cg} - R_x/2$, $x_2 = X_{cg} + R_x/2$. It leads to two uncoupled Schrödinger equations. The one for the internal coordinate R_x, with reduced mass $\mu = {}^1/_2 m_x$, force constant k_x and vibrational quanta $\omega' = (2k_x/m_x)^{1/2}$, reads

$$\left\{-\frac{1}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R_x^{\,2}} + \frac{k_x}{2}(R_x - R_e)^2 - \left(v + \frac{1}{2}\right)\omega'\right\}\Psi_v(R_x) = 0 \qquad (12)$$

All subsequent equations are as in the "I–X" case, but with replaced values for mass, $m_x \to \mu$, and frequency, $\omega \to \omega'$. So we obtain eq 13 instead of eq 7:

$$\Delta R_x = \sqrt{4S/(m_x \omega')} = \sqrt[4]{8S^2/(k_x m_x)} \qquad (13)$$

For X$_2$ molecules, there appears a *magnifying* factor of $(1/\underline{w})^{1/2} = 2^{1/2}$ in the formula with mass and frequency (handy for the spectroscopist) and a magnifying factor of $2^{1/4}$ in the formula with the basic physical parameters atomic mass and force constant.

2.5. Symmetric Digonal Molecule X–A–X. In terms of the X–X distance R_{xx}, the A–X bond length change is $\Delta R_x = 1/2\Delta R_{xx}$. If we take k_x as force constant for each A–X bond in X–A–X, the force constant for the X–X motion is $k_{xx} = {}^1/_2 k_x$. The reduced mass for the symmetric stretch, with A at rest, is $\mu = {}^1/_2 m_x$, as in the X–X case. The vibrational quantum $\omega' = [({}^1/_2 k_x)/({}^1/_2 m_x)]^{1/2}$ is $(k_x/m_x)^{1/2} = \omega$, as for the I–X single bond. The Schrödinger equation reads

$$\left\{-\frac{1}{m_x}\frac{\mathrm{d}^2}{\mathrm{d}R_x^{\,2}} + \frac{k_x}{4}(R_x - R_e)^2 - \left(v + \frac{1}{2}\right)\sqrt{k_x/m_x}\right\}\Psi_v(R_x) = 0 \qquad (14)$$

The respective eq 7 transforms with $k_x \to {}^1/_2 k_x$, $m_x \to {}^1/_2 m_x$, $\omega \to \omega$, yielding the X–X distance change $2\Delta R_x$, i.e.

$$\Delta R_x = \sqrt{S/(m_x \omega)} = \sqrt[4]{S^2/(k_x m_x)} \qquad (15)$$

This is *smaller* than eq 7 for I–X by a factor of $2^{1/2}$, and smaller than eq 13 for X–X by factors of $4^{1/2}$ and $8^{1/4}$.

We have similarly treated the cases X$_3$ (D_{3h}), AX$_3$ or X$_4$ (D_{3h}), X$_4$ (D_{4h}), AX$_4$ or X$_5$ (D_{4h}), X$_4$ (T_d), AX$_4$ or X$_5$ (T_d), X$_6$ (O_h), AX$_6$ or X$_7$ (O_h), X$_8$ (O_h), and AX$_8$ or X$_9$ (O_h). All coefficients were derived on several different paths to ensure them. The results are collected in Table 1, which gives the symmetry dependent correction coefficients for atomic weight $\underline{w} = m_{\mathrm{eff}}/m_x = (\Delta R_x^{\,\circ}/\Delta R_x)^2$ (where $\Delta R_x^{\,\circ}$ means the value obtained without the mass factor $\underline{w}$, sometimes suggested in the literature), for force constant $f = k_{\mathrm{eff}}/k_x$, and for vibrational quanta $q = (\omega'/\omega)^2$.

3. EXPERIMENTAL EXAMPLES

3.1. Two Cases of $D_{\infty h}$ Symmetry with Different Topological Factors: AX$_2$ and X$_2$. We will take uranyl $[\mathrm{OUO}]^{2+}$ and dinitrogen N$_2$ as examples of the AX$_2$ and X$_2$ cases, respectively. The famous absorption and luminescence of the uranyl ion[18] in the green region is of the single-electron type "O–U–O σ_u bonding" $\leftrightarrow$ "U-5f$\delta_u \phi_u$" nonbonding. It exhibits a progression (image in the Abstract)[19] of the linear stretching mode of the O-atoms with vibrational frequencies of $\sim$830 cm^{-1}

Table 1. Vibrational Quanta $\omega' = (qk_x/m_x)^{1/2}$ and Bond Length Changes $\Delta R_x = [2S\underline{w}^{-1}/(\omega' m_x)]^{1/2}$ upon Electronic Transition (in the Simplest Harmonic Approximation; See Text)^a

Molecule		Symmetry	$\underline{w}$	f	q^c
X_1 (reference)	$\underline{|-X}$	$C_{\infty v}$	- 1 -	- 1 -	- 1 -
X_2	X–X	$D_{\infty h}$	1/2	1	2
X_3 or AX_2	X–X–X	$D_{\infty h}$	2 ^{b}	2	<u>1</u>
X_3	△	D_{3h}	1	3	3
X_4 or AX_3	⅄	D_{3h}	3	3	<u>1</u>
X_4	□	D_{4h}	2	4	2 ^{d}
X_5 or AX_4	+	D_{4h}	4	4	<u>1</u>
X_4	empty	T_d	3/2	6	4
X_5 or AX_4	centered	T_d	4 ^{b}	4	<u>1</u>
X_6	empty	O_h	3	12	4
X_7 or AX_6	centered	O_h	6	6	<u>1</u>
X_8	empty	O_h	6	12	2
X_9 or AX_8	center	O_h	8	8	<u>1</u>

$^a k_x$ = single bond force constant, m_x = atomic mass of vibrating atom X, S = Huang–Rhys factor (all in au). In the Schrödinger equation, there appear the effective mass $m_{eff} = \underline{w}m_x$ and effective force constant $k_{eff} = f k_x$. ^{b}Neglected, i.e., set equal to $\underline{w}$ = 1, by Denning,[8] Ballhausen,[13,14] and others. ^{c}Supported by Fadini.[15] ^{d}Kohlrausch[16] (p 213) originally gave q = 4, but later[17] (p 70) gives q = 2.

in the ground state and of 700–750 cm^{-1} in the first excited state(s). The respective value of $(\omega' m_O)^{-1/2}$ is about 5 pm. During the last 50 years, different investigators applied different formulas to derive the "experimental" bond length changes:

(i) Already in 1962, Bartecki et al.[1] had investigated the spectra of uranyl nitrate in various solvents and derived $\Delta R_{U-O} \approx 22$ pm from a long progression with $S \approx 5$. Obviously they had applied some formula like $\Delta R_{UO} = \underline{(4S)^{1/2}} \times 5$ pm. In 1972, Wong et al.[20] deduced a bond length change of 10 pm ($\pm$1 pm) from the low-temperature fluorescence spectrum of cesium–uranyl–bromide crystals. In this compound, the first band is slightly stronger than the second one. The corresponding value of $S \approx 0.9$ is again consistent with a factor of $(4S)^{1/2}$.

(ii) Later and up to recently, Denning[8] derived bond length changes of various uranyl compounds from spectra of similar shapes and S values as in the image in the Abstract, but in the range of 7 pm ($\pm$1 pm), corresponding to a factor of $\underline{(2S)^{1/2}}$.

(iii) A recent experimental work used a factor of $\underline{(2\pi S)^{1/2}}$, deriving ΔR_x = 13–14 pm for a compound with an S value near 1.[21]

(iv) On the other hand, recently, quantum chemical ab initio calculations[12,22,23] of these uranyl bond length changes yielded ΔR_{U-O} values around 5 pm ($\pm$1/2 pm), which fits to a factor of $\underline{(1S)^{1/2}}$.

Different investigators applied different formulas, only the one with factor $(1S)^{1/2}$ being consistent, within a picometer, with eqs 10 and 11 containing the value $\underline{w}^{-1} = 1/2$ of linear X_3 or AX_2 molecules (Table 1). Neglecting the $\underline{w}$ factor increases the difference to 2 pm or more. Therefore, it must be admitted

that the computational agreement with our present theoretical derivation is a good indication, though no strict proof, for several reasons. First, differences of the order of a picometer are at the limit of both theoretical and experimental accuracies. Second, in our theoretical model, we have not yet considered frequency change and anharmonicity effects. Third, the lower excited states of uranyl are of near-degenerate $f\delta_u$ and $f\phi_u$ type (giving rise to strong configuration mixing and a breakdown of the independent particle model; see also below). Furthermore, related states of related compounds differ somewhat in their U–O equilibrium bond lengths. Therefore, after discussing an example for the other case of $D_{\infty h}$ symmetry, an X_2 molecule, we will analyze more impressive cases of higher symmetry (up to AX_6).

The experimental ionization spectrum of N_2 represents an accurately known X_2 case.[24] Though the first spectral feature, corresponding to the ionization of a nonbonding σ_g lone pair electron, is comparatively sharp, the second feature shows a long progression of the vibration of N_2^+ with $\omega_f \approx 1900$ cm^{-1} and $S \approx 1.2$. For $N_2 \rightarrow N_2^+$, ΔR_{NN} is known to be 7.7 pm from high resolution absorption spectroscopy. For the present case, $\underline{w}^{-1} = 2$ applies (Table 1), and then formula 11 yields 7.8 pm ΔR_x. Here we achieve an agreement of 0.1 pm among different experimental approaches, using our simple model including the topological $\underline{w}$ factor.

3.2. Two Cases of T_d Symmetry: AX_4 and X_4. In this section, the $[MnO_4]^-$, $[TcO_4]^-$, and P_4 species are discussed as examples for the AX_4 and X_4 cases. The permanganate ion has been investigated many times, because it is the paradigm of d^0 complexes.[25,26] An early discussion of the Mn–O bond expansion upon low-energy electronic singlet excitation $A_1 \rightarrow T_2$ (corresponding to the O-2p(t_1) $\rightarrow$ Mn-3d(e) one-electron transfer) was given by Ballhausen[13] in 1963. For ω' = 768 cm^{-1} and S = 1.73 ($\pm$0.2), one obtains a value of ΔR_{MnO} = 4.9 pm ($\pm$0.3 pm) from $\Delta R_x = [2\underline{w}^{-1}S/(m_O\omega')]^{1/2}$ with factor $\underline{w}$ = 4 (Table 1). ΔR_{MnO} = 5 pm had been derived from the experimental spectrum by Daul et al.[27] in 1997, whereas his quantum chemical calculation gave only 3.4 pm; i.e., the defect of the calculation is about 1.5 pm. Ziegler et al. found bond expansions of 3, 4, and 5 pm for the three lowest excited configurational states.[26] Remarkably, Ballhausen[13,14] had originally derived a much bigger value of 10 pm (neglecting the $\underline{w}$-factor, i.e., assuming $\underline{w}$ = 1). In 1987, Myrcek derived a similar value of 10.5 pm.[28] This large difference between the experimentally and computationally derived values sounds significant and in favor of the topological factor.

The lowest electronic excitations of MnO_4^- are of type HOMO(O2p-t_1) $\rightarrow$ LUMO(Mn3d-e) and are dominated by the symmetric breathing progression, but the next two sets of electronic excitations are of configuration-mixed types HOMO-1(O2p-t_2) $\rightarrow$ LUMO(Mn3d-e) and HOMO(O2p-t_1) $\rightarrow$ LUMO+1(Mn3d-t_2). The vibrational breathing progressions are strongly perturbed by Jahn–Teller splitting, vibronic coupling, and configuration mixing.[25] Although the validity of the simple model here becomes questionable, Ballhausen had derived a bond length expansion of 14 pm from ω' = 760 cm^{-1} and $S \approx 4$, though without the $\underline{w}$-factor, and later Myrcek similarly derived an "experimental" value of 16 pm.[28] Obviously, the approximate quantum chemical DFT results of 3–5 pm support much smaller values and thereby the $\underline{w}$-factor of 4.

An important intermediate in nuclear waste handling[29] is the pertechnetiate ion TcO_4^-.[30,31] The spectra and electronic states are similar to those of the permanganate ion. However, the spectroscopic Huang–Rhys factor of the first electronic excitation $A_1 \rightarrow T_2$ with $\omega \approx 800$ cm^{-1} is large, about $S \approx 4$, yielding a more significant result. With the factor $\underline{w}$ = 4, derive ΔR_{TcO} =

7 pm (± 1 pm). Our present quantum chemical ZORA DFT calculation with SAOP functional and valence TZ2P basis gave $\Delta R_{TcO} = 6$ pm (for computational details see the Supporting Information). Ziegler et al. obtained 4 and 5 pm for the two lowest excited configurations with a similar vibrational structure.[26] Without the $\underline{w}$-factor, one would obtain $\Delta R_{TcO} = 14$ pm, which significantly disagrees with the calculated values.

The P_4 molecule has T_d symmetry as MnO_4^- or TcO_4^- but without an atom in the center and with a different, much smaller topological factor of $\underline{w} = 1.5$. The third feature in the experimental photoelectron spectrum of P_4[32−34] at 11.8 eV corresponds to ionization from the $5a_1$-MO and exhibits a comparatively unperturbed progression of the symmetric breathing mode with $\omega' \approx 565 \pm 10$ cm^{-1} and $S \sim 1.1$. This gives $\Delta R_{PP} \approx 5.4$ pm expansion for the P−P bond length of about 219 ± 1 pm in the ground state.[33] Our DFT calculations yielded $R_{PP} = 220.8$ pm, $\omega' = 568$ cm^{-1}, and $\Delta R_{PP} = 4.1$ pm, increasing to 5.1 pm at the CCSD(T) level (for details see the Supporting Information file). This is a good agreement within the reliability ranges of a pm. In other words, the numerical quantum chemical results support the different $\underline{w}$-factors for same symmetry, but different topology.

3.3. Case of D_{4h} Symmetry: AX_4. An example of D_{4h} symmetry with same factor $\underline{w} = 4$ as for T_d symmetry (Table 1) is $[(UO_2)F_4]^{2-}$. Its photodetachment spectrum[35] shows a broad feature with $|E_{00} - E_{vert}| = 0.36$ eV. The symmetric vibrational stretching mode, basically of tetragonal (UO_2)−F breathing type, has a calculated ω' of 480 cm^{-1} (see the Supporting Information file) corresponding to $S \approx 6.5$. Formula 11 with $\underline{w} = 4$ yields $\Delta R_{UF} = 11 \pm 1$ pm, coinciding with the quantum chemically calculated value of 11 ± 1 pm. Neglecting the $\underline{w}$ factor would cause a deviation of 10 pm which corresponds to 10 standard deviations.

3.4. O_h Symmetry: AX_6. Octahedral molecules of AX_6 type are very common among the transition metal complexes. As an important compound in nuclear industry, UF_6 has been investigated intensively.[36] The first absorption band in the UV−vis spectrum[37] around 3.3 eV exhibits a breathing mode progression of $\omega' = 580-595$ cm^{-1}, with an S value around 3. With an atomic weight factor of $\underline{w} = 6$, one obtains $\Delta R_{UF} = 5.5 \pm 1$ pm, whereas without the w-correction one would obtain 13.5 ± 2 pm. The quantum chemically calculated value of $\Delta R_{UF} = 4$ pm (for details see the Supporting Information file) again supports definitely a large $\underline{w}$-factor.

4. CONCLUSIONS

Electronic spectra often exhibit vibrational progressions $v = 0 \rightarrow 0, 1, 2, \dots$ of the totally symmetric breathing mode. For the case of similar harmonic vibrational modes in the electronic initial and final states, the progression begins with band intensities $1:S:S^2/2$ and reaches its intensity maximum for $v_{max} \approx S - 1/2$.[a] From these rules of thumb, one can easily estimate the Huang−Rhys factor S and the change of bond length of the vibrating atom X upon electronic transition, $\Delta R_x = (\underline{w}^{-1})^{1/2}[2S/(\omega' m_x)]^{1/2}$, with a reasonable accuracy around a pm or 10%.

The second root factor in the formula is the common expression for a single bond. m_x is the mass of one of the equivalent atoms X of symmetric molecule AX_n or X_n. The "topological" first factor $(\underline{w}^{-1})^{1/2}$ takes into account that several masses are vibrating simultaneously, that there may be different numbers of bond forces, and that the direction of the vibrational motion may deviate from the bond direction. For the one dozen different cases investigated here and collected in Table 1, the topological factors take values between $8^{-1/2} \approx 0.35$ and $2^{1/2} \approx$

1.4. The quantitative agreement of the present theory and computations with experimental data within their standard deviations for such a wide range of factor values is hardly accidental or fortuitous, as suspected by some peers who do not "believe" in the $\underline{w}$ factor. The correctness of the $\underline{w}$ factor has been corroborated by comparison with both computational data and highly reliable alternative spectroscopic results.

We have shown for a set of molecules that only with the inclusion of $\underline{w}$ can one derive correct bond length changes from the experimental electronic spectra, which then become consistent with quantum chemical predictions. To achieve a better than picometer agreement, an analysis including S and $\underline{w}$ as well as the emission/absorption energy factors, different ω_i and ω_f, the anharmonicity, Dushinski rotations and vibronic couplings must be fully accounted for. However, this can only be achieved by more or less extended numerical computations.[38−43] Only in some restricted cases can some anharmonicity effects be accounted for analytically.[44,45]

On the other hand, some insight can already be gained from the simple model. One can give a simple rationalization for the $\underline{w}$-factor: Upon expansion of n equivalent bonds (for instance, 2 in X−A−X, 6 in $A(-X)_6$), the energy of the vertical excitation changes by n times the single-bond value. Accordingly, the observed vibrational progression becomes n times longer, the Huang−Rhys factor S is n times bigger and therefore must be reduced by factor $\underline{w}^{-1}$ to obtain the change ΔR_x of a single bond length. For molecules AX_n with an atom in the center, $\underline{w} = n$; otherwise $\underline{w}$ is smaller (Table 1). Formulas 2−5 are useful for a first estimate of the Huang−Rhys factor S, and formula 11 together with Table 1 may be useful for spectroscopists to derive a first estimate of ΔR_x. We stress again that our point was not improving spectra fitting somewhat, but correcting the physical interpretation and meaning of the common parameter values basically.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Table S1 (spectroscopic data of ground and first singlet excited states of TcO_4^-), Table S2 (optimized geometric parameters of the ground states of $UO_2F_4^{2-}$ and $UO_2F_4^-$), Table S3 (spectroscopic data of ground and first singlet excited states of UF_6), Table S4 (spectroscopic data of P_4 and P_4^+), a set of formulas concerning molecular vibrations, and the respective references. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ADDITIONAL NOTE

[a] This formula can, e.g., be derived from eq 2 by using the derivative $dx!/dx$ and Stirling's formula, which is accurate at the percent range even for small n values.

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