

Application of Intensity Sum Rules to the Atomic Tensors and the Dipole and Rotational Strengths Recently Calculated for NHDT

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IR and VCD intensity sum rules have been applied to the atomic tensors and the dipole and rotational strengths recently obtained by Jalkanen *et al.* [*J. Phys. Chem.* 92 (1988) 1781 and *J. Chem. Phys.* 90 (1989) 3204] for the chiral isotopomer of ammonia, NHDT. These authors calculated the atomic tensors with analytical derivative methods at the SCF level of approximation, and via nuclear shielding tensors at the SCF-RPA (random phase approximation) level of approximation. It is found that the intensity sum rules are fulfilled when origin-independent intensities are considered and when all the terms are calculated from the same set of atomic tensors; the data calculated via nuclear shielding tensors required, however, the inclusion of a translational correction for fulfilment in the IR case. The advantage of these intensity sum rules in the present application is that they offer convenient tests of the correctness of intensity calculations in IR and VCD for each given set of atomic tensors, and that they provide an accumulated effect of the basis set considered. For the largest basis sets there is reasonable agreement between results obtained with the two quantum-mechanical approaches.

The intensities of the t th fundamental transitions in infrared (IR) and vibrational circular dichroism (VCD) spectra can be rationalized in terms of the dipole strength, D_t , and the rotational strength, R_t , respectively.¹ Within the harmonic approximation for molecular vibrational motion expressions (1a) and (1b) hold for D_t ¹ and R_t ,²⁻⁶ in which

$$D_t = \frac{\hbar}{2} \frac{1}{\omega_t} \left(\frac{\partial \tilde{\boldsymbol{\mu}}}{\partial Q_t} \right)_0 \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_t} \right)_0 \quad (1a)$$

$$R_t = \frac{\hbar}{2} \left(\frac{\partial \tilde{\boldsymbol{\mu}}}{\partial Q_t} \right)_0 \left(\frac{\partial \boldsymbol{m}}{\partial Q_t} \right)_0 \quad (1b)$$

$\boldsymbol{\mu}$ and \boldsymbol{m} are the molecular electric and magnetic dipole moments, respectively, \dot{Q}_t is the time derivative of the t th normal vibrational coordinate, and ω_t is the corresponding fundamental frequency in radian s⁻¹. The scalar product is written here as a matrix product with the aid of the symbol $\tilde{}$, signifying transpose. The index ₀ refers to the equilibrium configuration of the molecule.

The derivatives in eqn. (1) can be expressed in terms of atomic polar tensors (APTs), $\mathbf{P}_{X(\mu)}^{(a)} = (\partial \boldsymbol{\mu} / \partial X^{(a)})_0$,⁷⁻¹¹ and atomic axial tensors (AATs), $\mathbf{P}_{X(m)}^{(a)} = (\partial \boldsymbol{m} / \partial X^{(a)})_0$,^{3-6,10-12} using eqns. (2a) and (2b), where N is the number of atoms

$$\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_t} \right)_0 = \sum_{a=1}^N \mathbf{P}_{X(\mu)}^{(a)} X_t^{(a)} \quad (2a)$$

$$\left(\frac{\partial \boldsymbol{m}}{\partial Q_t} \right)_0 = \sum_{a=1}^N \mathbf{P}_{X(m)}^{(a)} X_t^{(a)} \quad (2b)$$

and $X_t^{(a)}$ is the atomic displacement vector of atom a for normal mode t .

The APTs \mathbf{P}^a and AATs \mathbf{M}^a occurring in Stephens' formalism for VCD^{10,11} are related to those in eqn. (2) as in eqns. (3a) and (3b), where Im denotes the imaginary part

$$\mathbf{P}_{X(\mu)}^{(a)} = \tilde{\mathbf{P}}^a \quad (3a)$$

$$\mathbf{P}_{X(m)}^{(a)} = 2 \hbar \text{Im } \tilde{\mathbf{M}}^a \quad (3b)$$

(\mathbf{M}^a is purely imaginary).

For the three normal rotational coordinates and the three normal translational coordinates eqn. (2a) can be expressed as in eqns. (4a) and (4b), respectively, familiar

$$\langle (\boldsymbol{\mu}_0) \rangle \equiv \begin{bmatrix} 0 & \mu_{0z} & -\mu_{0y} \\ -\mu_{0z} & 0 & \mu_{0x} \\ \mu_{0y} & -\mu_{0x} & 0 \end{bmatrix} = \sum_{a=1}^N \mathbf{P}_{X(\mu)}^{(a)} \langle (\mathbf{q}_0^{(a)}) \rangle \quad (4a)$$

$$\mathbf{0}_3 = \sum_{a=1}^N \mathbf{P}_{X(\mu)}^{(a)} \quad (4b)$$

from the polar tensor IR intensity theory;^{7,8} see also Refs. 9 and 13. Here, $((\boldsymbol{\mu}_0))$ represents $\boldsymbol{\mu}_0$ expressed as an anti-symmetric second-rank axial tensor and $((\boldsymbol{q}_0^{(a)}))$ is defined analogously, where $\boldsymbol{q}_0^{(a)}$ is the equilibrium position vector of atom a . $\mathbf{0}_3$ is a 3×3 zero matrix. The analogous rotational and translational mode equations provided by eqn. (2b) have been derived recently by Buckingham *et al.*,⁴ as shown in eqns. (5a) and (5b); see also Ref. 6 for a derivation

$$\frac{1}{\hbar} \mu_N \mathbf{g}_0 \mathbf{I} = \sum_{a=1}^N \mathbf{P}_{\chi(m)}^{(a)} ((\boldsymbol{q}_0^{(a)})) \quad (5a)$$

$$-\frac{1}{2c} ((\boldsymbol{\mu}_0)) = \sum_{a=1}^N \mathbf{P}_{\chi(m)}^{(a)} \quad (5b)$$

within the localized molecular orbital (LMO) model. Here, μ_N is the nuclear magneton, \mathbf{g}_0 is the molecular g -value tensor^{14,15} and \mathbf{I} is the moment of inertia tensor; see Ref. 13, in particular eqn. (34), for the corresponding equations in Stephens' formalism. The electronic contribution to the left-hand side of eqn. (5a) can be expressed in terms of the paramagnetic susceptibility, χ^p , of the molecule.^{4,16,17} Analogous rotranslational sum rules occur in the formalism for nuclear shielding tensors^{18,19} from which the atomic tensors also can be obtained;^{4,17,20,21} see Ref. 13 for details.

In the polar tensor IR intensity theory Biarge *et al.*⁷ derived an intensity sum rule which takes into account the contributions from both the vibrational and the rotranslational modes. In their matrix formalism, and using the dipole strength D_i , this sum rule can be written as eqn. (6),

$$\begin{aligned} & \frac{\hbar}{2} \sum_{a=1}^N \frac{1}{m_a} \text{Tr} \left[\tilde{\mathbf{P}}_{\chi(\mu)}^{(a)} \mathbf{P}_{\chi(\mu)}^{(a)} \right] \\ &= \sum_{i=1}^{3N-6} \omega_i D_i + \frac{\hbar}{2} \text{Tr} \left[((\boldsymbol{\mu}_0)) ((\boldsymbol{\mu}_0)) \mathbf{I}^{-1} \right] \end{aligned} \quad (6)$$

where Tr signifies the trace of the matrix and m_a is the mass of atom a ; see also Refs. 8 and 22. The first, second and third terms will be denoted ΣA_l ($l = 1$ to $3N$), ΣA_l ($l = 1$ to $3N-6$) and ΣA_{R_ξ} ($\xi = X, Y, Z$), respectively. ΣA_{R_ξ} is often referred to as the rotational correction.

Polavarapu was the first to apply an analogous approach to the intensities in VCD.^{5,23} However, the sum rule equation obtained was evaluated within the fixed partial charge (FPC) model, and the conclusions drawn were not quite general. The present author arrived at the same sum rule equation, which was evaluated⁶ within the LMO model. Taking into account the general appearances of the symmetry invariant atomic tensors,²⁴ it was possible to formulate a general sum rule for ΣR_l ($l = 1$ to $3N$) for chiral molecules.²⁵ This sum was found to be zero only for certain

molecules made chiral by isotopic substitution. On the basis of the work of Buckingham *et al.*,⁴ a general expression can also be given for the rotational correction, ΣR_{R_ξ} ($\xi = X, Y, Z$).²⁵ The VCD intensity sum rule can be written as eqn. (7), where ΣR_l and ΣR_{R_ξ} is the first and last

$$\begin{aligned} & \frac{\hbar}{2} \sum_{a=1}^N \frac{1}{m_a} \text{Tr} \left[|\mathbf{A}_a| \tilde{\mathbf{P}}_{\chi(\mu)}^{(a)} \mathbf{P}_{\chi(m)}^{(a)} \right] \\ &= \sum_{l=1}^{3N-6} R_l + \frac{\hbar}{2} \text{Tr} \left[((\boldsymbol{\mu}_0)) \left(\frac{1}{\hbar} \mu_N \mathbf{g}_0 \mathbf{I} \right) \mathbf{I}^{-1} \right] \end{aligned} \quad (7)$$

term, respectively, and the various quantities are defined in eqns. (1b), (2), (4a) and (5a). The superscripts ⁰ occurring in the left-hand sides of eqns. (6) and (7) indicate that the atomic tensors there are referred to their respective atomic coordinate systems, where they have their simplest appearances,²⁴ and in eqn. (7) the determinant $|\mathbf{A}_a|$ of the 3×3 matrix transforming from the atomic coordinate system a to the common coordinate system reflects the axial nature of the AAT. For clarity, the left-hand side expression from eqn. (5a) is given within parentheses in the last term of eqn. (7). If desired, that term can be simplified using the relationship $\mathbf{I} \mathbf{I}^{-1} = \mathbf{E}_3$, a 3×3 unit matrix.²⁵

It should be pointed out that the rotational corrections in eqns. (6) and (7) are to be evaluated in a centre-of-mass coordinate system, and as a result that should hold also for the other terms in these equations. However, these terms are origin-independent (for inexact wavefunctions the VCD terms may be origin-dependent; see below). Also note that, since a mere rotation does not influence the trace, it is not necessary to use the principal axes for the evaluation of the rotational corrections if another centre-of-mass coordinate system happens to be more convenient.

Recently, Jalkanen *et al.*^{26,27} and Jalkanen *et al.*²⁸ have performed extensive *ab initio* quantum-mechanical calculations of the atomic tensors and D_i and R_i of the chiral isotopomer of ammonia, NHTD, within Stephens' formalism^{10,11} for VCD. This gives us an opportunity to apply the IR and VCD intensity sum rules. The application of the IR intensity sum rule is well-known,^{22,29} but is of interest here for a comparison. One reason for this is that most of the APTs in Ref. 28 do not fulfil eqn. (4b), i.e. for these atomic tensors the right-hand side of eqn. (4b) will deviate more or less from zero. As a result, the occurrence of *translational corrections* on the right-hand sides of eqns. (6) and (7) has to be considered. Since these intensity sum rules are based on linear transformations from derivatives with respect to the atomic displacement vectors, $\mathbf{X}^{(a)}$ (or $\dot{\mathbf{X}}^{(a)}$), on the left-hand sides to derivatives with respect to all the normal coordinates (or their time derivatives) on the right-hand sides (see the division of the atomic tensors into atomic vibration, rotation and translation tensors in Ref. 6), these translational corrections will take the form of eqns. (8) and (9). Here, $\tilde{\mathbf{T}} = (T_x, T_y, T_z)$ are the three normal

$$\sum_{\xi=X,Y,Z} A_{T_{\xi}} = \frac{\hbar}{2} \text{Tr} \left[\left(\frac{\partial \tilde{\boldsymbol{\mu}}}{\partial \mathbf{T}} \right)_0 \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{T}} \right)_0 \right] = \frac{\hbar}{2m} \text{Tr} \left[\tilde{\mathbf{0}}_3 \mathbf{0}_3 \right] \quad (8)$$

$$\begin{aligned} \sum_{\xi=X,Y,Z} R_{T_{\xi}} &= \frac{\hbar}{2} \text{Tr} \left[\left(\frac{\partial \tilde{\boldsymbol{\mu}}}{\partial \mathbf{T}} \right)_0 \left(\frac{\partial \mathbf{m}}{\partial \mathbf{T}} \right)_0 \right] \\ &= \frac{\hbar}{2m} \text{Tr} \left[\tilde{\mathbf{0}}_3 \left(-\frac{1}{2c} ((\boldsymbol{\mu}_0)) \right) \right] \end{aligned} \quad (9)$$

translational coordinates, and $\mathbf{0}_3$ and $-\frac{1}{2c}((\boldsymbol{\mu}_0))$ are defined in eqns. (4b) and (5b), respectively. Since $\mathbf{0}_3$ is a zero tensor, the translational corrections are clearly zero and therefore not included in the original intensity sum rules. However, in the present application, all the quantities in the rotational and translational corrections are replaced by the corresponding right-hand side expressions from eqns. (4) and (5). With this approach the translational correction may be non-zero when eqn. (4b) is not fulfilled, as further elucidated below.

Application of intensity sum rules to NHDT

The atomic tensors in Refs. 26–28 and 30 were calculated (A) with analytical derivative methods at the SCF level of approximation (operators μ and π)^{26,27,30} and (B) via nuclear shielding tensors at the SCF-RPA level of approximation (operators R, P, F and L, K).²⁸ Here, μ_{R} , π_{P} and F refer to the use of electronic position, momentum and force operators, respectively, to obtain the APTs, and π_{L} and K refer to the use of electronic angular momentum and torque operators, respectively, to obtain the AATs. The fulfilment of the rotranslational sum rules by these atomic tensors of ammonia and some other molecules has recently been examined by Stephens *et al.*¹³ and, for ammonia, by the present author.³¹ In the latter work a modified rotranslational sum rule from eqn. (50) of Ref. 6 was used, relating the APTs and AATs. It has the advantage of being origin-independent for ammonia and its isotopomers even if eqn. (4b) is not fulfilled. It should be mentioned that Stephens *et al.*¹⁷ have also applied the rotational sum rule in eqn. (5a) expressed in terms of the paramagnetic susceptibility, χ^p , and the electronic parts of the AATs, or the corresponding nuclear shielding tensors, to check the accuracy of the AATs of ethylene oxide. For the present application of intensity sum rules to ammonia it is of interest to know that only $\text{APT}(\mu)$ ^{26,27,30} fulfils eqn. (4b).^{13,31}

For the calculation of the intensities^{26–28} the various APTs were applied in eqns. (2a) and (1a), yielding $D_i(\text{A},\text{A})$ ($\text{A} = \mu_{\text{R}}, \text{P}, \text{F}$) for NHDT, and the various APTs and AATs were applied in eqns. (2) and (1b), yielding $R_i(\text{DO}, \text{A}, \text{B}, \text{C})$ ($\text{A}, \text{C} = \mu_{\text{R}}, \pi_{\text{P}}, \text{F}$) and ($\text{B} = \pi_{\text{L}}, \text{K}$), where A, B and C are the operators referred to above. [In $R_i(\text{DO}, \text{A}, \text{B}, \text{C})$ operator A characterizes the APT(A)s introduced via eqn. (2a) and operators B and C together define the AAT(DO,B,C)s

introduced via eqn. (2b) according to the so-called distributed origin (DO) with origins at nuclei gauge.]^{10,11,13} D_i is always origin-independent, while R_i , for inexact wavefunctions, is origin-independent only if $\text{A} = \text{C}$.²⁸

The other terms in the intensity sum rule equations were calculated here via the right-hand sides of eqns. (4) and (5) from the various atomic tensors in Refs. 27, 28 and 30, and the resulting tensors were thereafter introduced into eqns. (6)–(9) for further evaluation. These evaluations, as well as the numerical calculations, were performed with the use of the program Theorist³² for Macintosh. The quantities A and R obtained were multiplied by $\hbar e^2/\text{amu}$ and $\hbar e^2 a_0/c \text{amu}$,³³ respectively, for conversion from atomic units to Gaussian c.g.s. units. The evaluation of eqn. (9) showed that $\sum R_{T_{\xi}} = 0$ by symmetry for ammonia and its isotopomers, i.e. independently of whether the right-hand side of eqn. (4b) is zero or not. According to the sum rule given in Ref. 25 it also holds that $\sum R_i = 0$ for ammonia and its isotopomers. Thus for NHDT the VCD intensity sum rule in eqn. (7) is reduced to $\sum R_i = -\sum R_{R_{\xi}}$.

Applying the IR intensity sum rule, eqn. (6), to the tabulated $D_i(\text{A},\text{A})$ values ($\text{A} = \mu_{\text{R}}, \text{P}, \text{F}$) and the corresponding APTs from Refs. 27 and 28 gives a fulfilment only for $D_i(\mu, \mu)$, as should be expected. However, with the translational correction from eqn. (8) included, eqn. (6) is also fulfilled for $D_i(\text{A},\text{A})$ ($\text{A} = \text{R}, \text{P}, \text{F}$). The most relevant terms are displayed in Table 1 for the various basis sets.

The tabulated *origin-independent* $R_i(\text{DO}, \mu_{\text{R}}, \text{A}, \mu_{\text{R}})$ values ($\text{A} = \pi_{\text{L}}, \text{K}$) and the corresponding atomic tensors from Refs. 27 and 28 were all found to fulfil the VCD intensity sum rule in eqn. (7), as may be seen from Table 1.

Results and discussion

Considering first the IR intensities, we find from Table 1 that $\sum A_i(\mu, \mu)$ of data set (A) and the corresponding $\sum A_i(\text{R}, \text{R})$ of data set (B) differ for the smallest basis sets, and for these basis sets the translational correction of data (B), $\sum A_{T_{\xi}}(\text{R}, \text{R})$, is considerable; see in particular basis set DZ and note that three of the basis sets, DZ, DZ/1P and TZ/2P, are the same for data (A) and (B). Also note that $\sum A_{T_{\xi}}(\mu, \mu)$, not included in part (A) of Table 1, is zero for all basis sets, since $\text{APT}(\mu)$ fulfils eqn. (4b). However, $\sum A_i(\mu, \mu)$ of the largest basis sets of data (A) is in good agreement with $\sum A_i(\text{R}, \text{R})$ of the largest conventional basis set, LZ95, and the largest polarized basis sets of data (B), and for these basis sets $\sum A_{T_{\xi}}(\text{R}, \text{R})$ is practically zero. $A_i(\text{A}, \text{A})$ ($\text{A} = \text{P}, \text{F}$) of data (B) show larger deviations, and the translational corrections, $\sum A_{T_{\xi}}(\text{A}, \text{A})$, are small only for basis set LZ95, but about 10 (in the units of Table 1) for the largest polarized basis sets.

For the VCD intensities, we find that $\sum R_i(\text{DO}, \text{R}, \text{L}, \text{R})$ of data (B) is very large for the smallest conventional basis sets and varies much more with the basis sets than does the corresponding $\sum R_i(\text{DO}, \mu, \pi, \mu)$ of data (A). However, for the largest polarized basis set of data (B), DZ/POL, there

Table 1. Numerical values for NHDT^a of some relevant terms in the IR and VCD intensity sum rule eqns. (6) and (7). The translational correction required for the IR data (B) is defined in eqn. (8). The A quantities are in 10^{-24} esu² cm² s⁻¹, and the R quantities in 10^{-44} esu² cm².

(A)^b Data from Jalkanen *et al.*²⁷

Basis set ^c	ΣA_i^d	$(\Sigma A_i - \Sigma A_i - \Sigma A_{R_{\xi}})^d$	$\Sigma R_i(\text{DO})^e$	$\Sigma R_{R_{\xi}}(\text{DO})^e$
STO-3G	7.49	0.01	0.086	-0.085
3-21G	13.51	-0.02	0.136	-0.136
4-31G	16.18	0.01	0.163	-0.163
6-31G	16.57	0.00	0.171	-0.171
DZ	17.67	0.01	0.203	-0.293
6-31G*	13.47	-0.02	0.096	-0.006
6-31G**	12.89	0.02	0.093	-0.094
DZ/1P	13.83	0.01	0.114	-0.115
6-311G**	12.56	-0.01	0.082	-0.082
6-31G(EXT)	11.72	-0.01	0.076	-0.077
TZ/2P	12.37	0.00	0.089	-0.090
VD/3P	11.37	0.02	0.074	-0.074

(B)^b Data from Jalkanen *et al.*²⁸

Basis set ^c	ΣA_i^f	$(\Sigma A_i - \Sigma A_i - \Sigma A_{R_{\xi}})^f$	$\Sigma A_{T_{\xi}}^f$	$\Sigma R_i(\text{DO})^g$	$\Sigma R_{R_{\xi}}(\text{DO})^g$
DZ	61.41	503.48	503.47	7.8	-7.721
	74.29	664.65	664.68	12.1	-12.190
	1019.63	463.17	463.26		
DZ/1P	10.73	112.43	112.47	1.8	-1.963
	28.48	243.94	243.91	2.7	-2.689
	558.55	103.28	103.47		
LZ45	7.03	4.07	4.09	0.4	-0.361
	9.66	6.92	6.94	0.4	-0.452
	20.89	0.29	0.28		
TZ/2P	7.87	19.59	19.60	1.0	-0.960
	10.36	27.39	27.38	1.1	-1.072
	49.27	9.40	9.43		
LZ57	6.16	6.50	6.52	0.5	-0.452
	8.03	10.22	10.22	0.6	-0.502
	13.36	4.47	4.50		
LZ95	11.79	0.01	0.00	0.0	-0.040
	12.16	0.03	0.01	0.1	-0.034
	13.46	0.16	0.19		
VD/POL	4.33	2.25	2.27	0.1	0.014
	16.69	118.25	118.28	0.0	-0.042
	12.68	95.84	95.83		
VD/DZ/POL	14.87	0.06	0.07	0.1	-0.136
	12.80	64.61	64.63	0.1	-0.145
	11.44	63.04	63.04		
6-31G/POL	11.67	0.04	0.03	0.1	-0.142
	12.35	9.47	9.46	0.1	-0.150
	12.54	10.09	10.11		
DZ/POL	11.23	-0.02	0.02	0.2	-0.065
	12.72	14.40	14.43	0.0	-0.066
	12.58	14.15	14.13		

^aAccurate atomic masses and coordinates of NHDT are given in Refs. 26 and 28, respectively. ^bThe atomic tensors used have been calculated (A) with analytical derivative methods at the SCF level of approximation,^{27,30} and (B) via nuclear shielding tensors at the SCF-RPA level of approximation.²⁸ ^cThe basis sets of the data sets (A) and (B) are defined in Tables I of Refs. 26 and 28, respectively. ^dThe displayed quantities are $\Sigma A_i(\mu, \mu)$ (calculated from ω_i and D_i),²⁷ $\Sigma A_i(\mu, \mu)$ and $\Sigma A_{R_{\xi}}(\mu, \mu)$, as defined in the text. ^eThe displayed quantities are $\Sigma R_i(\text{DO}, \mu, \pi, \mu)$ (from R_i)²⁷ and $\Sigma R_{R_{\xi}}(\text{DO}, \mu, \pi, \mu)$, as defined in the text. ^fThe displayed quantities are $\Sigma A_i(A, A)$ (calculated from ω_i and D_i),²⁸ $\Sigma A_i(A, A)$, $\Sigma A_{R_{\xi}}(A, A)$ and $\Sigma A_{T_{\xi}}(A, A)$ with $A = R$ (first line), P (second line) and F (third line), as defined in the text. ^gThe displayed quantities are $R_i(\text{DO}, R, A, R)$ (from R_i)²⁸ and $\Sigma R_{R_{\xi}}(\text{DO}, R, A, R)$ with $A = L$ (first line) and K (second line), as defined in the text.

is reasonable agreement with ΣR_i of the largest data (A) basis sets [the low accuracy of the ΣR_i values of data (B) is due to the low precision of R_i given in Ref. 28; compare instead with $-\Sigma R_{R_{\xi}}$ from the last column]. For the smallest polarized basis set, VD/POL, the sign of $\Sigma R_{R_{\xi}}(\text{DO}, \text{R}, \text{L}, \text{R})$ [and probably also of $\Sigma R_i(\text{DO}, \text{R}, \text{L}, \text{R})$, if a higher precision had been used in Ref. 28] is opposite to that obtained with all the other basis sets. $\Sigma R_i(\text{DO}, \text{R}, \text{K}, \text{R})$ of data (B) is even larger for the smallest conventional basis sets, but for the other basis sets it shows behaviour similar to that of $\Sigma R_i(\text{DO}, \text{R}, \text{L}, \text{R})$; for a higher precision use instead $-\Sigma R_{R_{\xi}}(\text{DO}, \text{R}, \text{K}, \text{R})$ from the last column.

The IR translational correction, $\Sigma A_{T_{\xi}}$, gives in a single number a measure of the deviations from zero of the right-hand side of eqn. (4b). (It is proportional to the sum of the squares of the elements of the resulting tensor.) However, even if $\Sigma A_{T_{\xi}}$ is zero, as for APT(μ), fulfilment of the VCD intensity sum rule, eqn. (7), cannot be taken as evidence that the APTs and the corresponding AATs are mutually consistent. That can only be determined with the rotranslational sum rules [expressed here by eqns. (4a) and (5b)], as was done in Ref. 13, or with the use of eqn. (50) of Ref. 6, as was done in Ref. 31. In fact, APT(μ) and AAT(DO, π , μ) of ammonia are not consistent for the smallest basis sets. However, for the largest basis sets the deviations are small. It may therefore be concluded that the intensity sum rules, as applied here, are fulfilled even if the atomic tensors do not satisfy the rotranslational sum rules in eqns. (4) and (5). The reason is that all the terms in the intensity sum rules are calculated from the same set of atomic tensors, and that the atomic tensors used give origin-independent intensities. Thus, the usefulness of the intensity sum rules in this kind of application is rather that they offer convenient tests of the correctness of intensity calculations in IR and VCD for a given set of atomic tensors, and that they provide an accumulated effect of the basis set considered. For the largest basis sets there is reasonable agreement between results obtained with the two quantum-mechanical approaches, in particular when the electronic position operator, μ and \mathbf{R} in the two approaches, is used for calculating the APTs.

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