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Directional characteristics of the moments of the dipole-oscillator-strength distribution of molecules: H_2 and H_2O

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We report polarization propagator calculations within the random-phase approximation of several isotropic moments and their directional components of the dipole-oscillator-strength distribution of H_2 and of H_2O. The calculations show that there is strong dependence on the polarization direction of the incoming beam. The dependence of the moments on the molecular geometry is also discussed. In particular, the mean excitation energy for stopping is found to be very directionally sensitive, leading to the necessity of using directionally specific mean excitation energies when discussing oriented targets. It is possible that the sample phase dependence of the stopping power of water may be in part due to directional effects in I_0. A transferable bond mean excitation energy for the O—H bond is calculated, and is found to be constant within ±1% for $\sphericalangle$H—O—H from 95° to 120° at constant bond length R_{OH}. It agrees well with previous results.

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I. INTRODUCTION

The various energy-weighted moments of the dipole-oscillator-strength distribution (DOSD)

$$S(\mu)=\int E^{\mu}\frac{df}{dE}dE\ , \tag{1}$$

$$L(\mu)=\int E^{\mu}\ln E\frac{df}{dE}dE\ , \tag{2}$$

and the associated mean excitation energies

$$I_{\mu}=2R\ \exp[L(\mu)/S(\mu)] \tag{3}$$

of a molecule can be related to many aspects of the interaction of radiation with matter [1,2] such as the stopping and straggling of swift, massive projectiles, the Lamb shift, polarizabilities, refractivities and normal Verdet constants, and many more. In addition, they satisfy sum rules [3] which deepen understanding of the properties they describe. To calculate these moments, it is necessary to have access to the complete dipole-oscillator-strength distribution, as the moments are formed from sums over the entire energy spectrum of oscillator strengths $\{f\}$ and excitation energies $\{E\}$. Under most circumstances the appropriate moments to be used are the isotropic ones, comprising contributions from all polarizations, as there is generally no directional relation between the incoming beam and the symmetry axes of the target system. Experimental technology has improved so much in recent years, however, that questions of directional dependence of the moments of the DOSD have arisen. For example, consider the stopping (the property that we will be concerned with here) of a crystalline molecular solid. In this case, the molecular bonds will have a particular directional relationship to the velocity of the incoming particles, and one must consider the directional characteristics of the mean excitation energy (I_0, the appropriate moment to describe stopping, *vide infra*). A more dramatic example might be ultrathin films [4] where bonds can be lined up parallel to or perpendicular to the beam direction, again requiring investigation of the directional aspects of the moments of the DOSD.

The question then arises as to whether directional effects are large enough to cause physically observable phenomena. There has been very little work along these lines other than on the $S(\mu)$ [5] moments. There are, however, two theoretical and one semiempirical paper dealing with anisotropic stopping which treat it from very different perspectives. In a thorough analysis, Crawford [9] considered the stopping power in the high velocity (nonrelativistic) limit of a swift particle penetrating an anisotropic medium characterized by a frequency-dependent dielectric constant. He found a lateral force on the particle, and, more germane, a difference in stopping dependent on the directional relationship of the particle beam to the target molecular axes. In the case of protons impinging on graphite, this amounts to a difference of ~5–6% at a projectile energy $E_p=100$ keV, well within experimental reach. A very different approach was taken by Diercksen *et al.* [6], who used the polarization propagator scheme (*vide infra*) to calculate the spectral moments of the DOSD of N_2 directly by explicitly summing over the pseudostates. They found a difference between $I_{\parallel}$ and $I_{\perp}$ of nearly 20%, corresponding to a 10% difference in stopping. Finally, Kumar and Meath, using anisotropic DOSD constraint techniques [7], found a slightly smaller (15%) but still substantial anisotropy in I_0 (and other moments of the DOSD) for N_2. Thus all methods indicate that the directional dependence in stopping powers is experimentally accessible.

In the following, we report polarization-propagator [10] calculations [11] of the directional components of the moments of the DOSD with emphasis on the mean excitation energy for stopping, I_0.

II. METHODOLOGY

From the residues and poles of the polarization propagator

$$\langle\langle \alpha;\beta \rangle\rangle_E = \sum_{n(\neq 0)} \left[\frac{\langle 0|\alpha|n\rangle\langle n|\beta|0\rangle}{E-E_n+E_0} + \frac{\langle 0|\beta|n\rangle\langle n|\alpha|0\rangle}{E+E_n-E_0} \right] \tag{4}$$

one can obtain the transition moments (and thus oscillator strengths) and excitation energies, $E_n - E_0$, of the system directly, without explicitly generating the excited states of the system [10]. Here α,β are Cartesian components of the dipole-moment operator and the sum is over all excited states $|n\rangle$. The polarization propagator can be evaluated perturbatively at several levels of sophistication [10]. The zeroth-order approximation, generally taken to be the Hartree-Fock (HF) solution, takes both ground and excited states as simple, unrelaxed, single determinants of ground-state HF orbitals. Some correlation is introduced into the excited state when the propagator is approximated at the monoexcited configuration interaction (MECI) level. Both ground and excited states are correlated in the self-consistent first-order approximation to the propagator, the random-phase approximation (RPA). Our experience has consistently been that the propagator must be evaluated *at least* at the RPA level if properties of the DOSD [such as the Thomas-Reiche-Kuhn (TRK) sum rule] are to be represented accurately. Higher orders of approximation to the propagator are also extant, but require excessive computational effort for minor improvements in the property [12]. The calculations reported here are thus carried out in the RPA to the propagator.

The poles of the propagator give the excitation energies of the system

$$E_{0n} = E_n - E_0 \tag{5}$$

while the residues determine the Cartesian components of the oscillator strengths,

$$f_{0n}^{(\alpha)} = \tfrac{2}{3} E_{0n} \langle 0|\alpha|n\rangle\langle n|\alpha|0\rangle \ . \tag{6}$$

Using a finite basis set, as is the case here, results in a discrete representation of the continuum, allowing us to calculate the moments in Eqs. (1) and (2) by direct summation. The Cartesian components of the DOSD become

$$S_\alpha(\mu) = \sum_{n\neq 0} E_{0n}^{\mu} f_{0n}^{(\alpha)} \ , \tag{7}$$

$$L_\alpha(\mu) = \sum_{n\neq 0} (E_{0n}^{\mu} \ln E_{0n}) f_{0n}^{(\alpha)} \ , \tag{8}$$

and the associated mean excitation energies are

$$I_\mu^{(\alpha)} = 2R \exp\left[\frac{L_\alpha(\mu)}{S_\alpha(\mu)} \right] \ . \tag{9}$$

The total moments are then the sums of the components, and the directional mean excitation energies add as

$$\ln I_\mu = \frac{1}{S(0)} \sum_\alpha S_\alpha(0) \ln I_\mu^{(\alpha)} \ . \tag{10}$$

It is also possible to obtain the S and L of the DOSD *directly* from the propagator matrices, without going throughout the explicit sum over states. However, at the RPA level that we use here, it is equally easy to the sum over states, and the results are identical.

III. RESULTS AND DISCUSSION

A. H_2

The calculations on H_2 were carried out in the random-phase approximation, using a basis of 90 contracted Gaussian type orbitals (CGTO's) comprised of $[9s,6p,3d]$ atomic orbitals on each atom [13]. This basis has been shown to give good results for moment-related properties of H_2 [14]. It gives a value of the TRK sum rule, which is exact for a complete basis set in RPA, of 1.999 885 in the length formulation and 1.999 345 in the velocity formulation at the equilibrium internuclear distance of 1.4011 bohr. The agreement between the two formulations indicates that the basis is well balanced, and that both agree with the total number of electrons in the system indicates that the basis is reasonably complete, at least for properties of this sort.

Calculations were carried out in the RPA length formulation at several distances around the equilibrium value, and the energy-weighted moments of the DOSD and their components parallel and perpendicular to the molecular axis (z) are presented in Table I for several values of μ.

The behavior of the moments is consistent with the general structure of the DOSD. The spectrum of pseudostates for the transitions polarized perpendicular to the molecular axis ($\Pi \leftarrow \Sigma$) has components at higher energy than does the spectrum of pseudostates polarized along the molecular axis ($\Sigma \leftarrow \Sigma$). The $S(\mu)$ moments are sums of energy-independent transition moments, M_{0n}, weighted by $E^{\mu+1}$ [see Eqs. (6) and (7)]. Since $\mu > -1$ weights the high-energy region of the spectrum most, $S_\perp(\mu)$ would be expected to be larger than $S_\parallel(\mu)$ for positive μ. For $\mu < -1$, the opposite energy dependence is expected. There is no energy dependence in $S(-1)$, which is the simple sum of the transition moments, and $S(0)$ is governed by the TRK sum rule. This is consistent with the results in Table I.

A similar analysis pertains to the $L(\mu)$ moments, but the weighting factor is now $E^{\mu+1} \ln E$ [see Eqs. (6) and (8)]. Both $E^{\mu+1}$ and $\ln E$ weight the high-energy region more for $\mu > -1$, so for non-negative μ the perpendicular component of $L(\mu)$ should be larger, which is the case. For $\mu < -1$, the weighting factor falls from zero to negative infinity for $0 \leq E \leq 1$ due to the dominance of the ln$E$ factor at small E. Above 1, the factor rises to a broad maximum and then falls off as $E^{-(\mu+1)}$. Thus the high-energy region of the DOSD is weighted more heavily than the low and since the perpendicular DOSD has more transitions with excitation energies above 1 a.u., the perpendicular component of $L(-1)$ and $L(-2)$ is seen to be the larger. Thus, for $L(\mu)$ the perpendicular components are always larger, while for $S(\mu)$ this is only true for $\mu > -1$.

The mean excitation energies I_0 and I_{-1} are of interest as they are the material parameters that determine the stopping, or linear energy transfer, and straggling, or line broadening, of swift, charged particles by matter [15]. The calculated values of I_μ for $-2 \leq \mu \leq 1$ are presented in Table II. From Eq. (9) it can be seen that I_μ has only energy dependence of ln$E$ from $L(\mu)/S(\mu)$. Thus the high-energy part of the DOSD dominates, and $I_\perp$ should be larger than $I_\parallel$, as is indeed the case. Figure 1 depicts I_0 and its components as a function of the internuclear distance. It should be noted that the total mean excitation energy and its components are all rather strong functions of internuclear distance, and that there is a significant difference among the three components at all distances. Thus one would expect that in oriented targets where the projectiles sample only one polarization direction, it would be inappropriate to use the isotropic mean excitation energy in preference to, or in lieu of, the proper anisotropic value. An example is that mentioned above of ultrathin H_2 layers, where the molecules could be oriented either parallel or perpendicular to a particle beam.

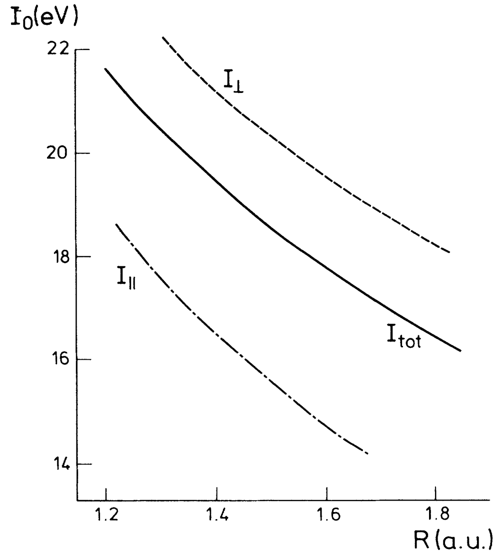

FIG. 1. Mean excitation energy of H_2 and its components as a function of internuclear distance.

The standard work on anisotropic moments of the dipole-oscillator-strength distribution of H_2 is that of Ford and Browne [16]. They report only the anisotropic $S(\mu)$ for $-2 \leq \mu \leq 0$, and their results are in agreement with those reported here to about 1.5%. They also report mean excitation energies, but not their anisotropic components [17].

TABLE I. Total and directional components of the energy-weighted moments of the DOSD of H_2 vs internuclear distance.

R (bohr)	0.70	1.10	1.4011	1.70	2.10
$S(1)$ (a.u.)	2.5042	1.9451	1.6693	1.4728	1.2902
$\parallel$	0.7444	0.5416	0.4485	0.3855	0.3309
$\perp$	0.8799	0.7018	0.6104	0.5436	0.4797
$S(0)$	1.9996	1.9998	1.9999	1.9999	2.0001
$\parallel$	0.6665	1.6665	0.6666	0.6666	0.6666
$\perp$	0.6666	0.6666	0.6667	0.6667	0.6667
$S(-1)$ (a.u.)	2.1019	2.6309	3.0540	3.4846	4.0650
$\parallel$	0.7356	0.9642	1.1596	1.3690	1.6667
$\perp$	0.6831	0.8334	0.9472	1.0578	1.1991
$S(-2)$ (a.u.)	2.5552	3.9180	5.2289	6.7785	9.2437
$\parallel$	0.9171	1.5174	2.1525	2.9637	4.3651
$\perp$	0.8190	1.0023	1.5382	1.9074	2.4393
$L(1)$ (a.u.)	1.0936	0.3464	0.0582	−0.1105	−0.2325
$\parallel$	0.1956	−0.0313	−0.0962	−0.1235	−0.1317
$\perp$	0.4490	0.1888	0.0772	0.0065	−0.0504
$L(0)$	0.1141	−0.3639	−0.6178	−0.9366	−1.2349
$\parallel$	−0.0091	−0.2066	−0.3362	−0.4491	−0.5774
$\perp$	0.0610	−0.0787	−0.1678	−0.2438	−0.3287
$L(-1)$ (a.u.)	−0.2871	−0.9165	−1.5035	−2.1689	−3.1653
$\parallel$	−0.1250	−0.4032	−0.6866	−1.0299	−1.5796
$\perp$	−0.0811	−0.2567	−0.4084	−0.5695	−0.7929
$L(-2)$ (a.u.)	−0.6244	−1.7242	−3.0096	−4.7507	−7.9165
$\parallel$	−0.2418	−0.7344	−1.3804	−2.3389	−4.2538
$\perp$	−0.1913	−0.4949	−0.8146	−1.2059	−1.8313

TABLE II. Mean excitation energies (eV) of H_2 for $R_{HH}=1.4011$ a.u.

μ	I_μ	$I_\mu^{\parallel}$	$I_\mu^{\perp}$
1	28.18	21.96	30.88
0	19.45	16.43	21.16
-1	16.63	15.05	17.68
-2	15.30	14.33	16.02

In a recent paper, Kumar and Meath [7] (KM) have used constrained dipole-oscillator-strength techniques [7,8] to calculate the anisotropic moments of the DOSD for H_2. The overall agreement between their results (see Tables 1–3 of Ref. [7]) and ours is good [19]. Generally, our values for $S(\mu)$, $L(\mu)$, and I_μ are a bit larger than those of KM for $\mu<0$ and are smaller for $\mu>0$, but the differences are typically of the order of a volt or less. It is difficult to contrast the two methods at this level of accuracy. Certainly the high-energy region of the DOSD generated in the polarization-propagator approximation is the least accurate part, so that moments that weight this region of the spectrum most ($\mu>-1$, *vide supra*) will be the least accurate. Thus one might expect the KM values for the $\mu=1$ moments to be the more accurate. On the other hand, no constraints are used in this calculation, while the KM DOSD is constrained to fit theoretical values of $S(\mu)$ for $-2\le\mu\le2$. In the present work, values of $S(0)$ are calculated, not obtained by requiring that the TRK sum rule be fulfilled. Similarly $S(-1)$, containing no energy dependence, is simply the sum of the appropriate calculated oscillator-strength distribution. In both the case of our calculation and that of KM, the pseudostate approach is used. KM use 10 pseudostates for each polarization direction, while the number of pseudostates in the present calculation is determined by the basis, which in this case includes 24 $\parallel$ and 9 each $\perp$ pseudostates. The two methods agree to within 1.3%. Finally, the calculations reported here are for fixed bond length. KM, however, use experimental data in the construction of the DOSD (although not for the constraints). Thus, their results might be more appropriately compared to vibrationally averaged moments. Such averaging can easily give a percent or so change in the moments [6]. In conclusion, the agreement between these results and those of KM seems to be very good.

B. H_2O

Calculations were carried out on water at various geometries (bond length $\equiv R_{OH}$ and $\measuredangle$H—O—H$\equiv\theta$) using the uncontracted, 101 functions ($15s,8p,4d/10s,3p$) Gaussian basis of Lazzeretti and Zanasi [20]. This basis has previously been shown to give good results for calculation of the DOSD of water [18,21]. Calculations were carried out in the RPA in the length formulation, and the results are presented in Tables III and IV. (The molecule lies in the x-z plane with the z axis as the C_2 symmetry axis.)

In Table III we present the directional components of the $S(\mu)$ moments for $-2\le\mu\le1$. For comparison we also include the Hartree-Fock results of Chipman, Kirtman, and Palke (CKP) [22] and the semiempirical results of Zeiss *et al.* (ZMMD) [23]. Our methods are poorest for $S(\mu)$ when μ is large and positive (see Ref. [18]), especially for $S(2)$, which we consequently do not report. We do agree, however, within $\sim5\%$ with the CKP results for $S(-1)$ and $S(1)$ and their directional components, and our agreement with ZMMD is a little better than is that of CKP.

TABLE III. Total and directional components of the moments of the DOSD of H_2O at $R_{OH}=1.811096$ a.u. and $\theta=104.4499°$.

		This work	CKP[a]	ZMMD[b]
$S(1)$	tot	96.015	92.5	95.60
	x	31.766	30.8	
	y	32.175	30.9	
	z	31.789	30.8	
$S(0)$	tot	10.007		10.00[c]
	x	3.323		
	y	3.359		
	z	3.323		
$S(-1)$	tot	7.042	8.23	7.23
	x	2.492	2.56	
	y	2.209	2.92	
	z	2.345	2.76	
$S(-2)$	tot	8.500		9.64
	x	3.059		
	y	2.617		
	z	2.837		

[a] Reference [22].
[b] Reference [23].
[c] Constraint of the calculation.

The variation of I_0 and its components as a function of R_{OH} for fixed angle is shown in Fig. 2. The mean excitation energy is a rather strong function of the internuclear distance over the range considered, with the direction perpendicular to the molecular plane having the largest mean excitation energy. The direction along the symmetry axis has the next largest, and the direction in the molecular plane perpendicular to the symmetry axis the smallest, mean excitation energy. The explanation of this behavior parallels that suggested in the case of H_2, namely, that there are higher-energy components in the DOSD for y polarization than for z polarization, or for x polarization. Since the mean excitation energy components

TABLE IV. Variation of the mean excitation energy (eV) of water and its components with geometry.

R_{OH} (a.u.)	θ (deg)	I_x	I_y	I_z	I_{total}
1.600	104.4499	73.63	79.42	76.50	76.47
1.775	104.4499	69.91	77.18	73.49	73.44
1.811 096	104.4499	69.21	76.76	72.87	72.91
1.905 601	104.4499	67.45	75.71	71.55	71.51
2.100	104.4499	64.21	73.80	69.06	68.96
1.775	120	68.37	76.97	74.82	73.31
1.775	115	68.84	77.08	74.45	73.34
1.775	100	70.39	77.22	73.04	73.51
1.775	95	70.92	77.27	72.52	73.53

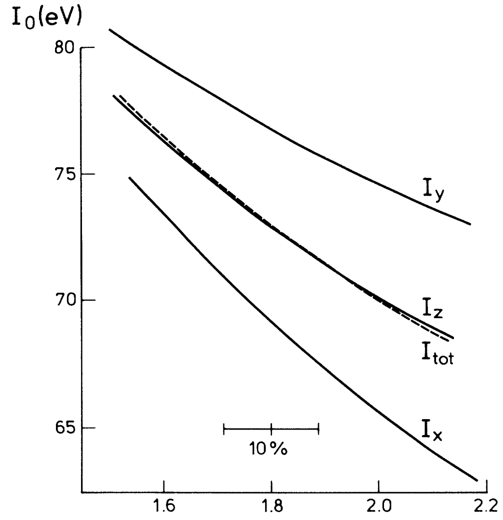

FIG. 2. Mean excitation energy of H_2O and its components as a function of R_{OH} for fixed $\theta = 104.4499°$.

add as in Eq. (10), the x and y components average, and the total I_0 behaves much like I_z. The changes in the components of the mean excitation energy with bond length are also explicable in terms of shifts in the DOSD with bond length.

A similar plot is given in Fig. 3 for the change of the mean excitation energy as a function of bond angle for fixed $R_{OH} = 1.775$ a.u. It is clear that the dependence of I_0 on angle is much weaker than that on bond length, as has been remarked previously [21]. In this case there is a reasonable variation in both I_z and I_x. The changes are, however, of opposite sense and the effects cancel out. Since I_y varies but little, the total mean excitation energy has only weak dependence on bond angle.

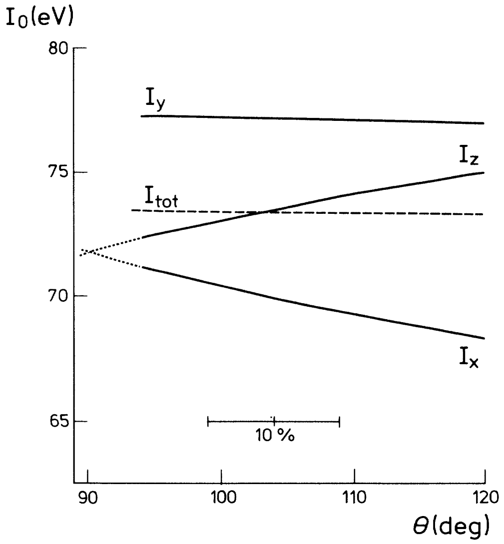

FIG. 3. Mean excitation energy of H_2O and its components as a function of θ for fixed $R_{OH} = 1.775$ a.u.

One might note here that there is perhaps a clue here as to why is an unexpectedly large phase effect observed in the stopping of water [24]. In ice, the bonds are both longer than in the isolated (gaseous) molecule and oriented with respect to the beam. Thus one might expect a difference of up to 5 eV between the main excitation energy appropriate to the oriented bonds in ice and that appropriate to water vapor, which could be a major contributor to the observed target phase difference in proton stopping.

C. Geometrical aspects of bond mean excitation energies

Recently we have had interest [25] in determination of transferable mean excitation energies and associated stopping powers of individual chemical bonds [26,27] which could be used additively in a Bragg-type rule to approximate the stopping powers of complicated or large molecules. Some isotropic bond mean excitation energies and stopping powers as a function of projectile velocity have previously been determined [26,27] using methods related to those reported here. However, as has been pointed out above, for oriented samples, the anisotropic mean excitation energies and stopping powers are the more appropriate, and we consider them here.

Consider a molecular bond in the xz plane of a space-fixed Cartesian coordinate system, A. In this coordinate system, the total mean excitation energy I has directional components $I = (I_x, I_y, I_z)$. Let B be another Cartesian coordinate system with its z axis directed along a molecular bond in the xz plane and its y axis collinear with the y axis in the A frame. In this (bond fixed) frame, the mean excitation energy is denoted $I_B = (I_B^x, I_B^y, I_B^z)$. Hence $I_y = I_B^y$. Assuming that the angle between the two z axes (and thus between the x axes as well) is ϕ, we find the relations between the other components of the mean excitation energy in the two coordinate systems by noting that the transition moments ($\mathbf{M}_{0n}$) are vector quantities. The oscillator strength along a polarization axis in A will then be

$$f_{0n}^{\alpha} \propto (M_{0n}^{\alpha})^2 \cos^2\phi \ , \qquad (11)$$

where α is the direction of the space-fixed axis and $\mathbf{M}_{0n}$ is the transition moment in the B frame. As there is no directional component in E_{0n}, then one would expect I to have the same directional as does f_{0n} [cf Eqs. (1) and (2)]. Thus

$$I_x = I_B^z \sin^2\phi + I_B^x \cos^2\phi \ , \qquad (12)$$

$$I_z = I_B^z \cos^2\phi + I_B^x \sin^2\phi \ . \qquad (13)$$

Rotation of H_2 up from the z axis in the xz plane gives the expected result: at 45° $I_x = I_z$, at 90° $I_x = I_B^z$ and $I_z = I_B^x$, and I_y and I_{tot} remain constant, independent of ϕ. This must, in fact, be the result, as it is a simple rotation of the molecule in the plane with no change of the bond itself, and calculation of the mean excitation energy for such a process is certainly independent of the choice of coordinate system.

We now wish to apply this idea to water with the purpose of determining a mean excitation energy and its directional components for the O—H bond that could be used in a Bragg-like rule.

The scheme will be to write the isotropic mean excitation energy I_0 and its Cartesian components (I_x, I_y, I_z) for a fixed bond length in terms of the bond mean excitation energy I_B and its components (I_B^x, I_B^y, I_B^z). We assume that as the bond angle of water is varied (i.e., the molecule is bent while maintaining the z axis as the C_2 symmetry axis), the change in the mean excitation energy arises from the change of relative orientation of the two bonds in the coordinate system, rather than from shifts in the DOSD attendant on alteration of the electronic structure of the molecule. The required bond mean excitation energies can then be extracted from the data in Table IV. The deviation of the derived bond mean excitation energies from constancy will provide a measure of goodness of the assumption that the changes are due to orientational effects alone, and the effect of the change of electronic structure on bending is minimal.

To implement this scheme, we first divide the molecule into core and bonding electrons (in this case, including the lone pairs). The total mean excitation energy of the system can then be written as [26]

$$\ln I_0 = \frac{1}{N}\left[\sum_{i}^{\text{cores}} N_C^i \ln I_C^i + \sum_{j}^{\text{bonds}} N_B^j \ln I_B^j\right] , \tag{14}$$

where N is the total number of electrons in the target, N_C^i is the number of electrons in each core (N_C in total), and N_B^j is the number of electrons in each bond (N_B in total). In the case of water, we consider the 1s core of two electrons and two identical bond functions of four electrons each. It should be remembered that the bond functions refer only to the valence electrons, and that the core electrons have been separated out. Combining this with Eqs. (10), (12), and (13), and assuming that the core electrons contribute equally to all three polarization directions ($N_C/3$ to each), we can write

$$\frac{N}{3}\ln I_x = \frac{N_c}{3}\ln I_C + \frac{N_B}{3}\ln\left[I_B^z \sin^2\frac{\theta}{2} + I_B^x \cos^2\frac{\theta}{2}\right] , \tag{15}$$

$$\frac{N}{3}\ln I_z = \frac{N_C}{3}\ln I_C + \frac{N_B}{3}\ln\left[I_B^z \cos^2\frac{\theta}{2} + I_B^x \sin^2\frac{\theta}{2}\right] , \tag{16}$$

and

$$\frac{N}{3}\ln I_y = \frac{N_C}{3}\ln I_C + \frac{N_B}{3}\ln I_B^y , \tag{17}$$

where θ is the $\sphericalangle$H—O—H and the z axis is the C_2 symmetry axis. For each value of θ we use the data in Table IV for I_x, I_y, and I_z as well as Hartree-Fock core mean excitation energies [28] to determine I_B^x, I_B^y, and I_B^z from Eqs. (15)–(17). We find that I_B and its components are nearly independent of θ. The average values for $R_{\mathrm{OH}} = 1.775$ a.u. and $95° \le \theta \le 120°$ are reported in Table V.

TABLE V. O—H bond mean excitation energy and its components (eV).

I_B^x	45.15
I_B^y	44.02
I_B^z	33.15
I_B	41.19

The variation in the values of the components of the bond mean excitation energy is ±1% over the range of angles considered. The bond mean excitation energy is nearly constant and apparently independent of electronic changes in the molecule on bending. The near invariance of I_y (see Table IV) on bending illustrates the same point.

Due to the lack of literature pertaining to this problem it is difficult to compare the result with other work. We have made a more empirical evaluation of the total bond stopping and mean excitation energy of the O—H bond [26] in the context of an ongoing program to determine transferable bond stopping cross sections for use in a Bragg rule, and the value there was found to be 40.68 eV, in good agreement with the value determined here.

IV. SUMMARY

The directional components of the moments of the DOSD of H_2 and water have been calculated, and it is found that there is significant difference among them. It is also found that they vary with internal coordinate with various strengths. The differences in the directional components of the moments as well as their variation with internal coordinate can be related to the relative shapes of the DOSD and to its shift with internal coordinate. The quantity of greatest interest to us, the mean excitation energy for stopping, is found to be strongly directionally dependent, leading to a strong directional dependence in the stopping cross sections of oriented targets. We therefore suggest that directional rather than isotropic mean excitation energies be used in the interpretation of experiments on anisotropic targets.

We show that it is possible to define a bond mean excitation energy for H_2O which is nearly independent of $\sphericalangle$H—O—H for angular variations between 95° and 120°. The same holds for its directional components. This is particularly interesting in view of the large variations in the total mean excitation energy and its components shown in Table IV. Such a transferable quantity is of use in a bond Bragg rule for calculation of stopping cross sections in large molecular targets. The value calculated here is in good agreement with the only other available value.

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