

## Geometric dependence of the mean excitation energy and spectral moments of water

Per Jensen

*Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, Germany*

Jens Oddershede and John R. Sabin

*Chemistry Department, Odense University, DK-5230 Odense M, Denmark*

*and Quantum Theory Project, Department of Physics, University of Florida, Gainesville, Florida 32611-2085*

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The spectral moments  $S(k)$  and  $L(k)$  of the dipole oscillator strength distribution of water have been calculated in the random-phase approximation as a function of molecular geometry. Several of the moments vary quite strongly with the O—H bond distance, while the dependence on bond angle is much less pronounced. In particular, the mean excitation energy is seen to change strongly with  $R_{OH}$ , being 72.92 eV when calculated at the molecular equilibrium geometry, and 71.61 eV in the vibrationally averaged ground state. Vibrationally averaged values of  $S(k)$ ,  $-6 \leq k \leq 1$ , are also reported along with the mean excitation energy for straggling,  $I_1$ .

### I. INTRODUCTION

In recent years the techniques used to measure the stopping of swift, massive particles by material foils have matured to the point where a reasonably small difference in stopping due to the chemical and physical state of the target can be measured.<sup>1</sup> One possible basis for these variations lies in the variation in the mean excitation energy ( $I_0$ ) of the target system with geometry, for example, that attendant on the geometrical differences between the free molecule in water vapor and the bound molecule in ice. Experimentally, differences in the stopping of water and ice have been found<sup>2</sup> to be some 10–12%. For a molecular solid such as ice, this is too much to be explained by the usual plasma frequency arguments.<sup>3</sup> Perhaps it is a geometry-based problem.

There have been few studies of the effect of geometry on mean excitation energies, and what work there is concentrated on diatomic molecules.<sup>4–7</sup> We wish, then, to investigate the dependence of the mean excitation energy of water on molecular geometry. The variation is found to be large enough so that comparison with experiment<sup>8</sup> should be with vibrationally averaged theoretical values, and we report those values here.

The mean excitation energy is only one of the many physical properties that can be extracted from the dipole-oscillator-strength distribution (DOSD) of a system,<sup>9</sup> and consequently we report several other moments as well.

### II. METHODOLOGY

We consider the DOSD of a system defined by the set of all excitations with excitation energies  $\{E_{0n}\}$  and associated oscillator strengths  $\{f_{0n}\}$ . The spectral moments of the DOSD are then defined by

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

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

where the integral encompasses all excitations, discrete and continuous. The associated mean excitation energies

(in atomic units) can then be obtained as

$$I_\mu = \exp[L(\mu)/S(\mu)]. \quad (3)$$

To evaluate these moments one needs the complete sets of excitation energies  $\{E_{0n}\}$  and oscillator strengths  $\{f_{0n}\}$  for the system. These we obtain, in the dipole length formulation, as the residues and poles of the polarization propagator, defined as<sup>10,11</sup>

$$\langle \langle r_a; r_b \rangle \rangle_E = \sum_{n \neq 0} \left[ \frac{\langle 0 | r_a | n \rangle \langle n | r_b | 0 \rangle}{E - E_n + E_0} - \frac{\langle 0 | r_b | n \rangle \langle n | r_a | 0 \rangle}{E + E_n - E_0} \right], \quad (4)$$

where  $r_a$  is a component of the dipole operator. From the poles  $E_{0n} = E_n - E_0$  and the residues  $\langle 0 | r | n \rangle$  the dipole length oscillator strengths can be calculated

$$f_{0n}^L = \frac{2}{3} \langle 0 | r | n \rangle \cdot \langle n | r | 0 \rangle (E_n - E_0), \quad (5)$$

where all quantities are in hartree atomic units.

We solve the equation of motion for the propagator perturbatively, using the fluctuation potential as the perturbation.<sup>10</sup> Experience shows<sup>6,7,12,13</sup> that correlation is needed in order to calculate reliable spectral moments of the DOSD. One needs to calculate the propagator at least in the consistent first-order approximation, which is identical to the random-phase approximation (RPA). The RPA adds correlation in both ground and excited states in a balanced way.

The polarization propagator is evaluated using a finite basis set, which yields a finite number of excitations equal to the number of allowed particle-hole excitations. As a result, we approximate the continuum with a finite number of discrete excitations placed such that they represent the continuum. We have found this to work well<sup>6</sup> for cases such as the present one, where we evaluate quantities which depend on sums over all excited states. However, no physical significance can be attached to individual continuum pseudostates obtained in this way.

The basis used in these calculations is the uncontracted (15s, 8p, 4d/10s, 3p) Gaussian basis of Lazzeretti and

Zanasi,<sup>14</sup> which we have previously used<sup>6</sup> for calculations on water. The set consists of 101 functions and admits 418 particle-hole excitations.

### III. RESULTS

A criterion of basis-set quality for calculations of second-order dipole transition properties such as the DOSD is the fulfillment of the Thomas-Reiche-Kuhn (TRK) sum rule. For the dipole length oscillator strengths [Eq. (5)] and their velocity formulation analogs<sup>15</sup>

$$f_{0n}^V = \frac{2}{3} \langle 0 | \mathbf{p} | n \rangle \cdot \langle n | \mathbf{p} | 0 \rangle / (E_n - E_0), \quad (6)$$

one then has

$$S^L(0) = \sum_{n \neq 0} f_{0n}^L, \quad (7a)$$

$$S^V(0) = \sum_{n \neq 0} f_{0n}^V. \quad (7b)$$

The TRK sum rule then states that, for a complete basis,

$$S^L(0) = S^V(0) = N, \quad (8)$$

where  $N$  is the total number of electrons in the system. For a finite basis, then, the agreement of  $S^L(0)$  with  $S^V(0)$  indicates how well the tight and diffuse functions in the basis are balanced, while agreement of the two formulations with  $N$  gives an indication of the completeness of the basis. In a complete basis set the fulfillment of the TRK sum rule does not depend on geometry, and changes in  $S(0)$  attendant on changes in geometry are attributable to the slight changes in the basis set caused by moving the atom centered functions. At a standard water geometry<sup>14</sup> of  $R_{\text{OH}} = 1.811096$  a.u. and  $\Theta = 104.4489^\circ$ , we calculate  $S^L(0) = 10.007$  and  $S^V(0) = 9.945$  indicating that the basis is both well balanced and (for dipole transitions) reasonably complete.

The sum rules  $S(k)$  and  $L(k)$  have been calculated at 20 different geometries with  $R = R_{\text{OH}}$  and  $\Theta = \Theta_{\text{HOH}}$  being varied separately and jointly. In Table I we present

TABLE I. Variation of  $S(\mu)$ ,<sup>a</sup>  $L(\mu)$ ,<sup>a</sup> and  $I_\mu$ <sup>b</sup> with molecular geometry.

$\Theta$	104.5°	104.5° <sup>c</sup>	104.5°	95.0°	120.0°
$R$ (a.u.)	2.10	1.811	1.775	1.775	1.775
$S(1)$	95.689	96.016	96.118	96.102	96.227
$S(0)$	10.008	10.007	10.006	10.007	10.006
$S(-1)$	7.787	7.042	6.953	6.945	6.979
$S(-2)$	10.750	8.500	8.267	8.229	8.367
$S(-3)$	18.870	12.968	12.440	12.310	12.773
$S(-4)$	38.341	23.341	22.133	21.715	23.182
$S(-5)$	88.229	47.838	44.907	43.640	48.165
$S(-6)$	224.222	109.010	101.371	97.647	111.386
$L(1)$	339.107	388.751	339.273	338.843	340.942
$L(0)$	9.302	9.863	9.940	9.948	9.920
$L(-1)$	-1.152	-0.152	-0.045	-0.031	-0.085
$L(-2)$	-4.945	-2.738	-2.542	-2.492	-2.667
$I_1$	941.504	926.780	926.305	924.724	940.791
$I_0$	68.930	72.915	73.482	73.535	73.331

<sup>a</sup>In a.u., dipole length formulation.

<sup>b</sup>In eV.

<sup>c</sup>Standard geometry for the isolated molecule.

data at several representative points<sup>16</sup> for  $S(\mu)$ ,  $L(\mu)$ , and  $I_\mu$  calculated in the dipole length formulation. It is clear that there is significant variation of the spectral moments of the DOSD with geometry, and that the variation is more strongly dependent on  $R$  than on  $\Theta$ . However, the TRK sum rule [ $S(0)$ ] is nearly geometry independent, thus substantiating the completeness of the basis set. In Fig. 1 we plot  $I_0(R)$  for fixed  $\Theta$ , and  $I_0(\Theta)$  for fixed  $R$  to illustrate the difference in  $R$  and  $\Theta$  dependence of one of the spectral properties. Although the  $R$  and  $\Theta$  coordinates are in no way equivalent, they are both plotted approximately  $\pm 10\%$  from equilibrium.

The moments with large negative  $k$  are most sensitive to geometrical variation. This is because the large negative powers of  $E_{0n}$  place most emphasis on the low-lying, or valence, excitations, and it is the valence and low-lying virtual orbitals that change most with geometry.

We expect the moments with  $\mu \leq 0$  to be most reliable since the moments for  $\mu > 0$  place emphasis on the high-energy excitation involving high-lying virtual orbitals, and those are the most poorly represented in a finite basis set. Similarly, the moments with smaller  $|\mu|$  should be most reliable, as large  $|\mu|$  magnifies any error in the valence excitation energies, for example, those arising from lack of second- and higher-order electron correlation effects in RPA.

As there is a significant variation of  $I_0$  and the spectral moments with geometry, comparison with experiment should be made with vibrationally averaged theoretical numbers. Thus we vibrationally averaged the mean excitation energies and spectral moments using the Morse-oscillator-rigid-bender internal-dynamics (MORBID) approach of Jensen,<sup>17</sup> employing a potential energy function determined by fitting to experimental energy spacings.<sup>18</sup> In this method the values for a particular moment are fitted to a polynomial of the form

$$f(\rho, r_1, r_3) = \sum_j \sum_{k \leq l} C_{jkl} \sin \rho (\cos \rho_e - \cos \rho)^j \times [(r_1 - r_e)^k (r_3 - r_e)^l + (r_1 - r_e)^l (r_3 - r_e)^k], \quad (9)$$

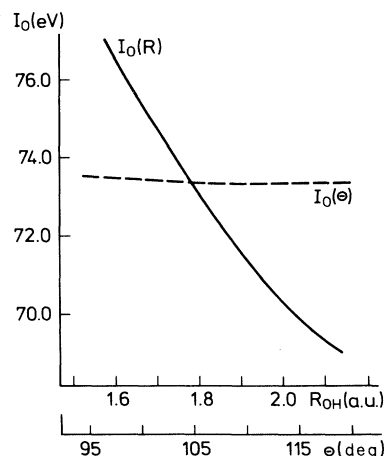


FIG. 1. Variation of  $I_0$  with molecular geometry.  $I_0(R)$  for fixed  $\Theta = 104.5^\circ$  and  $I_0(\Theta)$  for fixed  $R = 1.775$  a.u.

where  $r_1$  and  $r_3$  refer to the two O—H bond distances, respectively,  $\rho$  is the supplement of the angle  $\Theta$ , and subscripts  $e$  refer to quantities at the equilibrium geometry. The  $J=0$  vibrational wave functions are calculated by the MORBID method<sup>17</sup> and the appropriate matrix elements are then determined.<sup>19</sup>

The resulting vibrationally averaged quantities are given in Table II for the ground state and the fundamentals. Comparing the vibrationally averaged ground-state values to the values calculated at the fixed standard geometry, we find the same trend as before: the greatest changes are for largest  $|\mu|$ . Comparison of the vibrational averages for the fundamentals to those for the ground state shows that the vibrational average changes much more by exciting the stretching vibration than the bending. This is independent of which of the stretching modes is excited, and is consistent with our earlier observation that the moments are more strongly dependent on  $R$  than on  $\Theta$ .

#### IV. DISCUSSION

There are several experimental values of  $I_0$  with which we can compare, but the best, most generally accepted, value is that of Zeiss *et al.*,<sup>20</sup> who use an empirical scheme based on photoabsorption and fast-electron inelastic-scattering data for dilute water vapor to construct a DOSD and extract  $I_0$  from it. Their value of 71.62 eV is primarily derived from experiments and thus, in some manner, represents a vibrational average. It is in nearly perfect agreement with our ground-state vibrational average. Thermal vibrational averaging would not be expected to alter this value, as the lowest excited state (0,1,0) is 1594  $\text{cm}^{-1}$  above the ground state ( $e^{-\Delta E/kT} \approx 10^{-4}$ ) and the higher states all be above 3500  $\text{cm}^{-1}$  above ground. There are other experimental values which do not agree so well with ours, including one derived from stopping power measurements by fitting<sup>21</sup> (approximately 60 eV), and an older value of Zeiss *et al.*<sup>22</sup> (70.8 eV). There are also a few theoretical values available such as the equilibrium geometry value we have calculated with the same basis (72.92 eV),<sup>6,23</sup> and a value ob-

TABLE II. Vibrational averages ( $J=0$ ) of the mean excitation energies<sup>a</sup> and various moments<sup>b</sup> of the DOSD for the ground and fundamental levels.

State <sup>c</sup>	$A_1(0,0,0)$	$A_1(1,0,0)$	$A_1(0,1,0)$	$B_2(0,0,1)$
Energy <sup>d</sup>	0	3656.32	1594.25	3755.72
$I_0$	71.61	71.32	69.42	71.51
$I_1$	920.90	927.97	892.99	926.14
$S(1)$	94.89	94.99	92.04	95.26
$S(-1)$	7.04	7.12	6.84	7.14
$S(-2)$	8.66	8.95	8.44	8.96
$S(-3)$	13.55	14.37	13.23	14.39
$S(-4)$	24.98	27.17	24.43	27.17
$S(-5)$	52.48	58.66	51.44	58.51
$S(-6)$	123.38	143.07	121.48	142.94

<sup>a</sup>In eV.

<sup>b</sup>In a.u.

<sup>c</sup>States labeled by their total vibrational symmetry and by the number of quanta in the  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  modes.

<sup>d</sup>In  $\text{cm}^{-1}$ , above ground state.

tained from molecular sum rules and atomic data (71.35 eV).<sup>24</sup>

The ground-state vibrationally averaged mean excitation energy for straggling  $I_1$  is found to be 920.90 eV, also in excellent agreement with the Zeiss *et al.*<sup>20</sup> value of 931.4 eV and Peek's value<sup>5</sup> of 919.0 eV.

There are several calculations of the spectral moments of the DOSD, as many of them have direct connection to measurable properties and thus generate some interest.<sup>9</sup> In Table III we recapitulate some of them. The only reported spectral moments for a wide range of  $\mu$  are those of Zeiss *et al.*,<sup>20</sup> who extract moments from their experimental DOSD for  $-14 \leq \mu \leq 2$ . Although we have calculated values for  $\mu=2$  and could easily for  $\mu < -6$ , we do not report them as the reliability of our calculations decreases for large  $|\mu|$  (*vide supra*). We agree quite well with experimental values down to  $\mu=-4$ , but the results deteriorate for  $\mu=-6$ . Again this is due to the magnification of errors in the excitation energies due to the factor  $E_{0n}^\mu$  in the moment. We attribute deterioration of the  $S(k)$  moments for large, negative  $k$  to lack of post RPA correlation. We do agree with the experimental numbers quite a bit better than either of the other calculations, however. The calculations by Mulder and Meath<sup>25</sup> and by Chipman, Kirtman, and Palka<sup>24</sup> utilize certain sum rules to calculate the moments as ground-state averages of electric moment operators, and are restricted to  $-1 \leq k \leq 2$ . Both groups of authors use a self-consistent field (SCF) ground-state average and Chipman, Kirtman, and Palka use a VB ground state as well. None of the calculations is correlated, and all are calculated at a single geometry. Thus the differences between their calculations and ours can be attributed to these two factors. [In the limit of a complete basis the calculation of certain  $S(k)$  is equivalent when performed as a SCF ground-state average or as a sum over RPA generated states.<sup>25</sup> Thus, since none of these authors use a complete basis, it is a matter of semantics whether these

TABLE III. Comparison of some moments<sup>a</sup> of the DOSD.

	This work <sup>b</sup>	Zeiss <i>et al.</i> <sup>c</sup>	Mulder and Meath <sup>d</sup>	Kirtman, Chipman and Palka <sup>e</sup> MO	VB
$S(1)$	94.89	95.60	92.57	92.5	90.5
$S(0)$	10.01 <sup>f</sup>	10 <sup>g</sup>	10 <sup>g</sup>		
$S(-1)$	7.04	7.32	8.20	8.23	7.98
$S(-2)$	8.66	9.64			
$S(-3)$	13.55	16.75			
$S(-4)$	24.98	24.01			
$S(-5)$	52.48				
$S(-6)$	123.38	229.9			

<sup>a</sup>In a.u., dipole length formulation.

<sup>b</sup>Ground state [ $A_1(0,0,0)$ ] vibrational average.

<sup>c</sup>Reference 20.

<sup>d</sup>Reference 25.

<sup>e</sup>Reference 24. MO denotes molecular orbital. VB denotes valence bond.

<sup>f</sup>Not vibrationally averaged. The variation in  $S(0)$  is less than 0.005 over the range of geometries considered (see Table I).

<sup>g</sup>Constraint on the determination.

differences are attributed to lack of correlation or basis set effects.] As Chipman, Kirtman, and Palka<sup>24</sup> obtain only 59.6 eV for  $I_0$  and 988 eV for  $I_1$ , similar differences in the other spectral moments are not unexpected.

### V. CONCLUSIONS

The polarization propagator at the RPA level of approximation, when accompanied by vibrational averaging of the results, seems to provide an accurate and straightforward method for calculating the spectral moments of the DOSD and the associated mean excitation energies. The mean excitation energies for stopping and straggling are found to be  $I_0 = 71.61$  eV and  $I_1 = 920.9$  eV, respectively, vibrationally averaged in the ground state, in excellent agreement with the best available experimental results of Zeiss *et al.*<sup>20</sup> Agreement of our calculated moments with those of Zeiss *et al.* is best for small  $|\mu|$ , with some deterioration for the large negative moments.

Many of the spectral moments, and thus their associated mean excitation energies, show a strong dependence on geometry. In the case of water, the variation with bond length is much greater than with bond angle. This is quite different than the case of the magnetic susceptibility and rotational g factor in  $\text{NH}_3$ ,<sup>26</sup> where the angular dependence dominates. Thus one must be very careful in drawing conclusions about which internal modes effect a given property most strongly.

If one considers the static values of  $I_0$  calculated at the geometry of the isolated water molecule<sup>27</sup> and at the geometry of ice, where the bond angle remains about the

same but the bond length increases by  $\sim 0.05$  Å,<sup>28</sup> one calculates  $I_0^{\text{molecule}} = 72.92$  eV while  $I_0^{\text{ice}} = 71.51$  eV in the dipole length formulation at the RPA level. This is clearly not enough difference to give the observed<sup>2</sup> phase difference in proton stopping. The solution to this problem is thus not in the change in mean excitation energy attendant on bond length, but must lie elsewhere: perhaps in the hydrogen bonding in ice.

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<sup>16</sup>Data for all 20 geometries are available from the authors on request.

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