DIPOLE OSCILLATOR STRENGTH DISTRIBUTIONS AND PROPERTIES FOR METHANOL, ETHANOL AND PROPAN-1-OL AND RELATED DISPERSION ENERGIES

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Dedicated to Professor Joseph Paldus, a colleague and friend for a long time, on the occasion of his 70th birthday.

Recommended isotropic dipole oscillator strength distributions (DOSDs) have been constructed for the methanol and ethanol molecules through the use of quantum mechanical constraint techniques and experimental dipole oscillator strength (DOS) data; the DOS data employed are recent experimental results not available at the time of the original constrained DOSD analysis of these molecules. The constraints are furnished by molar refractivity data and the Thomas–Reiche–Kuhn sum rule. The DOSDs are used to evaluate a variety of isotropic dipole oscillator strength sums, logarithmic dipole oscillator strength sums, and mean excitation energies for the molecules. Pseudo-DOSDs for these molecules, and for propan-1-ol based on an earlier constrained DOSD analysis for this molecule, are also presented. They are used to obtain reliable results for the isotropic dipole-dipole dispersion energy coefficients C_6, for the interactions of the alcohols with each other and with 36 other species, and the triple-dipole dispersion energy coefficients C_9 for interactions involving any triple of molecules involving methanol, ethanol and propan-1-ol.

Keywords: Alcohols; Dipole properties; Pseudo states; Dipole-dipole and triple-dipole dispersion energies; Long range additive and non-additive interaction energies; DOSD; *Ab initio* calculations.

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One of the purposes of this paper is to assess the reliability of the results for a wide variety of the isotropic dipole properties of the ground states of the methanol, ethanol and propan-1-ol molecules evaluated previously[1] by using the constrained dipole oscillator strength distribution (DOSD) technique[2–7]. The original constrained DOSD calculations[1] were based on the then rather sparse and disjointed (as a function of photon energy) experimental dipole oscillator strength (DOS) data for these alcohols which were drawn from the work of several different experimental groups. Our new calculations for methanol and ethanol are based on much more recent, extensive and reliable experimental DOS data[8,9]. They can be used to directly check the reliability of the original DOSD calculations for these two molecules and to indirectly assess the reliability of the analogous results for propan-1-ol. We also present new reliable results for the isotropic dipole-dipole dispersion energies for the interaction of the three alcohols with each other and with a variety of other species. Discrete pseudo-state representations[10,11] of the recommended constrained dipole oscillator strength distributions for the alcohols are constructed which are useful for the efficient evaluation[10–12] of the dipolar dispersion energies, particularly the triple-dipole dispersion energies, for interactions involving these molecules; explicit reliable results for the triple-dipole dispersion energy coefficients are included for all triples of alcohol molecules.

The relationship between molecular dipole oscillator strength distributions (DOSDs) and the isotropic dipole properties of molecules, and the dipole-dipole and the triple-dipole dispersion energies for interactions involving molecules, is well known[2,13–19]. The molecular dipole properties explicitly considered here are the dipole oscillator strength sums S_k, the logarithmic dipole sums L_k, the mean excitation energies I_k, and the molar refractivity R_λ as a function of wavelength λ. The properties S_k, L_k and I_k, which depend on the value of the index k, and the dipolar dispersion energies find application in many research areas[2,13–16,20–32].

A quantum mechanical constraint technique[2–7] is used to construct the DOSDs for methanol and ethanol from a base of experimental dipole oscillator strength input data[1,8,9] using constraints comprised of the molar refractivity[1,33] of the molecules for two well separated wavelengths and the Thomas–Reiche–Kuhn sum rule[14,34] for the DOSDs. Specific results for integrated dipole oscillator strengths for these alcohols, over various energy regions, are computed. Recommended values for the dipole sums, S_k, $k = -10(2)-4(1)-3(1/2)0, 1, 2$, the logarithmic dipole sums L_k and mean excitation energies I_k, $k = -2(1)2$, and the molar refractivities of methanol and ethanol are tabulated; those for propan-1-ol can be found in the literature[1].

A ten pseudo-state representation of the recommended DOSD for each of the three alcohols is also constructed and tabulated and these are used to evaluate the results for the dipole-dipole dispersion energy coefficients for a variety of interactions involving these molecules, and the triple-dipole dispersion energy coefficients for the interaction of any combination of three alcohols. The estimated uncertainties in our results for the dipole properties and dispersion energies, and a comparison with literature values, are included in the discussion. The values obtained from the constrained DOSD approach, either the original[1] or the present calculations, are either the only values or the only reliable values, available for most of the dipole molecular properties considered in this paper. The results for the dispersion energies obtained herein are generally the only available reliable values for the interactions considered in this paper.

COMPUTATIONAL METHODS

The differential dipole oscillator strength distribution for a molecule is the differential dipole oscillator strength $\mathrm{d}f/\mathrm{d}E$ as a function of photon energy E from the electronic absorption threshold E_0 for the molecule to very high photon energies. Generally the dipole properties and dispersion energy coefficients evaluated using DOSDs are isotropic results since only orientationally averaged input dipole oscillator strengths are available over the required wide range of photon energies. In some instances[35–39], i.e. CO, H_2, N_2, NO and O_2, sufficient anisotropic constraints are available to permit the construction of anisotropic DOSDs and hence the evaluation of anisotropic molecular properties.

A variety of important isotropic molecular properties can be evaluated as integrals whose integrands involve the isotropic DOSD weighted by simple functions of the photon energy. These include the dipole oscillator strength sums S_k, the logarithmic dipole sums L_k, and the mean excitation energies I_k, defined by[2,13,14]

$$S_k = \int_{E_0}^{\infty} (E/E_\mathrm{H})^k (\mathrm{d}f/\mathrm{d}E)\,\mathrm{d}E \tag{1}$$

$$L_k = \int_{E_0}^{\infty} (E/E_\mathrm{H})^k (\mathrm{d}f/\mathrm{d}E) \ln(E/E_\mathrm{H})\,\mathrm{d}E \tag{2}$$

$$I_k = E_\mathrm{H} \exp(L_k/S_k) \tag{3}$$

where $E_H \approx 4.35975 \times 10^{-18}$ J ≈ 27.21 eV is the atomic unit of energy. The index k can take on various integer and half integer values and each choice defines a different dipole property via Eqs (1)–(3). For example: the straggling (I_1 and S_1), stopping (I_0), and the total (I_{-1}, S_{-1}) inelastic scattering cross-sections of fast charged particles in matter[13,20,21]; S_2 and I_2 determine[2,13,14] charge densities at the nucleus and Lamb shifts; while S_{-1}, S_{-3}, $S_{-3/2}$, S_{-2} and L_{-2} can be used to obtain estimates for the dipole-dipole dispersion energies between molecules[10,15,22,23]. An important property, which is involved as a constraint in the construction of DOSDs, is the molar refractivity R_λ of a dilute molecular gas. It is related[2,14–16] to the refractive index $n(\lambda)$ of the gas at wavelength λ and to an integral involving the DOSD:

$$\begin{aligned} R_\lambda &= (1/\rho)[(n^2(\lambda) - 1)/(n^2(\lambda) + 2)] \\ &= (4\pi/3)\, N_A (E_H)^2 a_0^3 \int_{E_0}^{\infty} (\mathrm{d}f/\mathrm{d}E)(E^2 - (hc/\lambda)^2)^{-1}\, \mathrm{d}E \\ &= (4\pi/3)\, N_A\, \alpha(\lambda) \end{aligned} \qquad (4)$$

where a_0 (bohr) ≈ 5.29177×10^{-11} m, ρ is the molar density of the gas, h is Planck constant, N_A is Avogadro constant, c is the speed of light and $\alpha(\lambda)$ is the frequency-dependent electronic dipole polarizability of the molecule. The static dipole polarizability is $\alpha_d = \alpha(\lambda = \infty) = a_0^3 S_{-2}$. The S_k, $k = -4$, -6, -8, ... are other moments of the DOSD that occur in the Cauchy expansion of $\alpha(\lambda)$.

The orientation-averaged dipole-dipole dispersion energy[16,17] for the interaction of molecules A and B is given by $C_6(\mathrm{A,B})R_{\mathrm{AB}}^{-6}$ where R_{AB} is the distance between species A and B and $C_6(\mathrm{A,B})$ is the dipole-dipole dispersion energy coefficient for the interaction

$$C_6 = E_H\, a_0^6 (3/2) \int_{E_0(\mathrm{A})}^{\infty} \mathrm{d}E(\mathrm{A}) \int_{E_0(\mathrm{B})}^{\infty} \mathrm{d}E(\mathrm{B}) \frac{[\mathrm{d}f(\mathrm{A})/\mathrm{d}E(\mathrm{A})][\mathrm{d}f(\mathrm{B})/\mathrm{d}E(\mathrm{B})](E_H)^3}{E(\mathrm{A})E(\mathrm{B})[E(\mathrm{A}) + E(\mathrm{B})]} \qquad (5)$$

where $E(\mathrm{A})$, $\mathrm{d}f(\mathrm{A})/\mathrm{d}E(\mathrm{A})$, and $E_0(\mathrm{A})$ are the excitation energy, the differential dipole oscillator strength, and the electronic absorption threshold for molecule A, respectively. The triple-dipole dispersion energy[16,18,19] for the interaction of three species A, B and C has the form $C_9(\mathrm{A,B,C})[3\cos\theta_A\cos\theta_B\cos\theta_C + 1]R_{AB}^{-3}\,R_{AC}^{-3}\,R_{BC}^{-3}$ where θ_A is the angle between R_{AB} and R_{AC} and the triple-dipole dispersion energy coefficient C_9 is given by a triple integral analogue of the double integral in Eq. (*5*), where the integrand contains the product of the DOSDs for molecules A, B and C with a function of the excitation energies $E(\mathrm{A})$, $E(\mathrm{B})$ and $E(\mathrm{C})$.

The dipole-dipole dispersion energy is the dominant interaction energy at long range for interactions of spherically symmetric systems including freely tumbling molecules. Its importance lies in its use for representing long range interactions between two atoms or molecules and in constructing potential energy models that are valid for all intermolecular distance[24–30]. Analogously, the triple-dipole dispersion energy gives the dominant non-additive interaction energy for an assembly of well-separated "tumbling" species and can be used to help model non-additive effects for other molecular configurations as well[26,31,32].

The basic procedure used here for constructing molecular dipole oscillator strength distributions (DOSDs) has been discussed in detail in the literature[2,6,7]. Briefly, the initial DOS data is divided, from the UV absorption threshold E_0 to very large values of the photon energy, into N_0 energy intervals as suggested by the structure of the input DOS data and by the photon energy regions associated with the individual sources of the DOS input data. The number of different initial DOSDs that can be obtained by taking all possible combinations of the input DOS data is given by[40] $N_D = \prod_{j=1}^{N_0} N_j$, where N_j is the number of independent sources of DOS data used for the j-th input spectral region. Each of the initial DOSDs considered is modified by requiring satisfaction of the constraints via application of the constrained least squares technique[2,6,7]. The input initial oscillator strength data base, $(\mathrm{d}f/\mathrm{d}E)_{\mathrm{initial}}$ vs E, for each spectral region i, is modified via

$$(\mathrm{d}f/\mathrm{d}E)^i_{\mathrm{constrained}} = (1+a_i)(\mathrm{d}f/\mathrm{d}E)^i_{\mathrm{initial}}\ , \quad i = 1, 2, \ldots, N_0 \tag{6}$$

so that the total constrained DOSD satisfies the imposed constraints through the choice of the a_i. The degree of modification of the initial DOSD data required to satisfy the constraints can be represented by the standard deviation (STD) defined by[6,40]

$$\mathrm{STD} = [\sum_{i=1}^{N_0}(a_i - \bar{a})^2 \ / \ N_0]^{1/2} \tag{7}$$

where $\overline{a}$ is the average of all the a_i values. The recommended DOSD is represented by a set of data points E_j and $(\mathrm{d}f/\mathrm{d}E)_j$, for $j = 1, 2, \ldots, N_p >> N_0$, and a set of interpolating functions to connect the points. For very high photon energies, $E \geq 10^8$ eV, $(\mathrm{d}f/\mathrm{d}E)$ is represented by the Born dipole formula[34] $AE^{-2.5}$. The dipole properties of molecules are readily evaluated[2] using such a representation of DOSDs.

CONSTRUCTION OF THE DOSDs

The experimental dipole oscillator strength (DOS) data used by Jhanwar and Meath[1] for constructing the original constrained DOSDs for methanol, ethanol and propan-1-ol have been reviewed by these authors. Generally relatively few sources of DOS data were available at that time, there was gap in the experimental DOS methanol data in the important photon energy region between 21 and 30 eV, generally the experimental DOS data were sparse as a function of photon energy, and no direct experimental data were available for $E > 100$ eV. We base our new constrained DOSD calculations for methanol and ethanol on the extensive DOS data of Brion and co-workers[8,9] which are available from the electronic absorption threshold to 360 eV for methanol and to 200 eV for ethanol; both high- and low-resolution measurements are available for $E < 30$ and 32 eV, respectively, while for higher photon energies only low-resolution measurements are available. Analogous experimental studies have unfortunately not been carried out for propan-1-ol. For methanol and ethanol, these more recent DOS results represent extensive collections of experimental DOS data from the same laboratory that in the past has produced DOS data for other molecules that have proved to be very reliable in the sense that the modifications in the data induced by our constraint procedures have often been less than or of the order of the estimated experimental errors of ≈5% (to 10%) (see, for example, refs[41–48]).

For higher photon energies, for which the recent experimental DOS data are not available, we use as input DOS values for each alcohol the recommended values of Jhanwar and Meath[1]. These were originally based on additivity rules and then modified by the constraints imposed on the overall initial DOS data collection. For large photon energies the modifications are generally quite small[1].

Reliable refractive index data for the gaseous alcohols are apparently only available for methanol[1,33]. As detailed below, and following the earlier work[1], additivity rules are used to generate the molar refractivity constraints for the higher alcohols and we use the explicit results of Jhanwar and Meath[1] for ethanol in what follows.

Methanol

The constraints for constructing various DOSDs for methanol are provided by the Thomas–Reiche–Kuhn sum rule S_0 = 18 and by experimental molar refractivity data. For methanol, the refractive index has been measured by Ramaswamy[33] for wavelengths varying from 4359 to 6440 Å. The molar refractivity R_λ for a dilute gas, as a function of wavelength λ, is related to the refractive index $n(\lambda)$ as discussed earlier. The R_λ values, corresponding to the experimental refractive index data[33] are given in the third column of Table II. The values of R_λ at the experimental wavelength extremes, namely $R(\lambda = 6440 \text{ Å}) = 8.3516 \text{ cm}^3 \text{ mol}^{-1}$ and $R(\lambda = 4359 \text{ Å}) = 8.5434 \text{ cm}^3 \text{ mol}^{-1}$, are employed as constraints for constructing the DOSD. The percentage difference between these two values of R_λ, namely $\Delta R_\lambda = 200\,(R_{\lambda_2} - R_{\lambda_1})/(R_{\lambda_1} + R_{\lambda_2}) = 2.3\%$, is much larger than the expected experimental error in the refractive index data and hence the least-squares constraint procedure[2,6,7] can be used with confidence with this refractivity data to construct the DOSDs for methanol[40,49].

The following DOSDs have been constructed for methanol:

DOSD1: 6.12–30.0 eV (high-resolution data of Burton et al.[8]); 30.0–360.0 eV (low-resolution data of Burton et al.[8]); 360 eV–∞ (recommended DOSD of Jhanwar and Meath[1]). STD = 4.82.

DOSD2: As in DOSD1 except the high-resolution data are replaced by the low-resolution data. STD = 3.96.

DOSD2, with the smallest STD, is chosen as the recommended DOSD for methanol. The integrated dipole oscillator strengths for the recommended DOSD, together with those calculated from the initial DOS data used to construct the DOSDs for methanol, are given in Table I. The approach used here removes errors in the initial DOSD data in a global sense and is capable of yielding reliable dipole molecular properties and very reasonable integrated oscillator strengths. It does not necessarily lead to constrained DOSDs that are accurate on a point-by-point basis[50].

Relative to our recommended results, the integrated DOS values calculated using the initial high resolution DOS data of Burton et al.[8] are low by about 70, 33 and 9% in the energy regions 6.1–7.4, 8.5–9.0 and 24–27 eV, respectively, and are high by 14% for 8–8.5 eV. In the other energy regions for which high-resolution data are available, the corresponding integrated DOSs agree with our recommended results to essentially within the esti-

TABLE I
Integrated dipole oscillator strengths[a] for CH_3OH

Energy region eV	Recomended DOSD2	Uncon-strained DOSD2	High-resolution data of Burton et al.[8]	Low-resolution data of Burton et al.[8]	Jhanwar and Meath[1]
6.122–7.4	1.533(–2)	1.624(–2)	4.646(–3)	1.624(–2)	5.820(–3)
7.4–8.0	2.457(–2)	2.580(–2)	2.413(–2)	2.580(–2)	2.851(–2)
8.0–8.5	2.749(–2)	2.848(–2)	3.143(–2)	2.848(–2)	3.695(–2)
8.5–9.0	3.319(–2)	3.413(–2)	2.230(–2)	3.413(–2)	2.509(–2)
9.0–10.0	9.766(–2)	1.020(–1)	9.510(–2)	1.020(–1)	1.094(–1)
10.0–11.8	3.448(–1)	3.525(–1)	3.262(–1)	3.525(–1)	3.856(–1)
11.8–13.0	4.059(–1)	3.934(–1)	3.894(–1)	3.934(–1)	4.265(–1)
13.0–14.0	4.560(–1)	4.323(–1)	4.548(–1)	4.323(–1)	4.609(–1)
14.0–15.0	4.997(–1)	4.678(–1)	4.937(–1)	4.678(–1)	4.839(–1)
15.0–16.0	4.954(–1)	4.626(–1)	4.632(–1)	4.626(–1)	4.559(–1)
16.0–17.0	4.981(–1)	4.649(–1)	4.729(–1)	4.649(–1)	4.666(–1)
17.0–18.0	4.911(–1)	4.593(–1)	4.618(–1)	4.593(–1)	5.162(–1)
18.0–19.0	4.797(–1)	4.497(–1)	4.492(–1)	4.497(–1)	4.515(–1)
19.0–20.0	4.669(–1)	4.399(–1)	4.496(–1)	4.399(–1)	4.483(–1)
20.0–21.0	4.437(–1)	4.203(–1)	4.279(–1)	4.203(–1)	4.411(–1)
21.0–22.0	4.200(–1)	3.999(–1)	4.043(–1)	3.999(–1)	4.295(–1)
22.0–23.0	3.920(–1)	3.753(–1)	3.767(–1)	3.753(–1)	3.967(–1)
23.0–24.0	3.618(–1)	3.482(–1)	3.467(–1)	3.482(–1)	3.673(–1)
24.0–27.0	9.725(–1)	8.918(–1)	8.851(–1)	8.918(–1)	8.781(–1)
27.0–30.0	7.624(–1)	7.178(–1)	7.135(–1)	7.178(–1)	7.371(–1)
30.0–35.0	9.902(–1)	9.285(–1)		9.285(–1)	9.567(–1)
35.0–40.0	7.597(–1)	7.291(–1)		7.291(–1)	7.433(–1)
40.0–50.0	1.089	1.041		1.041	1.058
50.0–70.0	1.260	1.215		1.215	1.547
70.0–100.0	9.175(–1)	9.010(–1)		9.010(–1)	1.039
100.0–300.	1.509	1.481		1.481	1.421
300.0–360.	5.498(–1)	5.467(–1)		5.467(–1)	4.703(–1)
360.–500.	6.165(–1)	6.127(–1)			6.127(–1)
500.–700.0	1.030	1.020			1.020
700.–1000.	7.449(–1)	7.396(–1)			7.396(–1)
1000–∞	8.455(–1)	8.386(–1)			8.386(–1)

[a] Numbers in parentheses indicate a power of ten.

mated experimental uncertainties of ≈5% and are generally lower than the recommended results. The initial low-resolution[8] integrated DOSs are about 8% lower than our recommended value for the energy region 24–27 eV. Otherwise they agree, to essentially within the experimental error of ≈5%, with our recommended results for the integrated DOSs over the entire range of photon energies, 6.1–360 eV, for which the experimental data are available. Generally speaking, the low-resolution integrated DOSs are lower than our recommended results for $E > 11.8$ eV; for lower photon energies they are higher than our recommended results. Table I also contains the integrated DOSs for the original recommended constrained DOSD for methanol constructed by Jhanwar and Meath[1]. The discrepancies with our recommended integrated DOSs are often less than 5% and generally less than about 10% with exceptions of –62, +16, +34, –24, +23, +13 and –15% for 6.1–7.4, 7.4–8.0, 8.0–8.5, 8.5–9.0, 50–70, 70–100 and 300–360 eV, respectively. The discrepancies vary in sign as E changes and so while they can be relatively large for some energy regions they do tend to cancel as the regions are expanded. For example, for the first three photon energy regions mentioned above, the total integrated DOSs vary by only 6%. Since the dipole properties calculated using DOSDs are integrals over photon energy that involve the differential dipole oscillator strengths, these discrepancies tend to cancel with the result that many of the properties calculated using the recommended DOSDs of this work and of the earlier alcohol paper[1]

TABLE II
Recommended values of the molar refractivity (in cm^3 mol^{-1}) of CH_3OH (ideal gas, STP) evaluated using the recommended DOSD2 and a comparison with literature values

λ, Å	Recomended DOSD2	Ramaswamy[33]
6709	8.3394	
6440	8.3516	8.3516[a]
5893	8.3822	
5462	8.4133	8.4120
5087	8.4475	8.4443
4917	8.4660	
4801	8.4796	8.4808
4359	8.5434	8.5434[a]
2302	9.7620	

[a] Used as constraints in constructing the DOSD.

agree quite well with each other (see below). Many sources of DOS data for methanol were involved in the construction of the original constrained DOSD for this molecule. These and other DOSs, and associated integrated DOSs, for the molecule have been discussed extensively earlier (see, for example, refs[1,8] and papers cited therein).

Ethanol

The constraints for constructing the DOSDs for ethanol are provided by the Thomas–Reiche–Kuhn sum rule $S_0 = 26$ and molar refractivity data generated[1] by using additivity principles. As discussed previously[1], there is apparently no (reliable) experimental refractive index data for gaseous ethanol. Several additivity rules for obtaining the molar refractivity of ethanol from that for methanol have been investigated and, following Jhanwar and Meath[1] who discuss the implementation of the result, we use values of the molar refractivity of ethanol obtained from

$$R_\lambda(\mathrm{C_2H_5OH}) = R_\lambda(\mathrm{CH_3OH}) + R_\lambda(\mathrm{C_3H_8}) - R_\lambda(\mathrm{C_2H_6}) \qquad (8)$$

and the results for 6440 and 2302 Å, namely 13.1134 and 15.3399 $\mathrm{cm^3\ mol^{-1}}$, respectively, are used as constraints to construct our recommended DOSD for ethanol. The percentage difference between these two values of R_λ is 15.5% and is much larger than the expected experimental error in the refractive index data.

The following DOSDs have been constructed for ethanol:

DOSD1: 6.082–32.0 eV (high-resolution data of Feng and Brion[9]); 32.0–200.0 eV (low-resolution data of Feng and Brion[9]); 200 eV–∞ (recommended DOSD of Jhanwar and Meath[1]). STD = 2.91.

DOSD2: As in DOSD1 except the high-resolution data are replaced by the low-resolution data. STD = 1.16.

DOSD2, with the smallest STD, is chosen as the recommended DOSD for ethanol. The integrated dipole oscillator strengths for the recommended DOSD, together with those calculated from the initial DOS data used to construct the DOSDs for ethanol, are given in Table III.

Aside from the energy regions 6.1–7.4 and 7.4–10.3 eV, where the discrepancies are –35 and –8%, respectively, the integrated DOSs evaluated using the initial high-resolution DOS data of Feng and Brion[9] agree with our recommended results to well within the estimated experimental errors of ≈5%. The discrepancies remain negative and steadily decrease in magnitude as E increases until they become positive, 1.7 and 3.6%, respectively, for

TABLE III
Integrated dipole oscillator strengths[a] for C_2H_5OH

Energy region eV	Recomended DOSD2	Unconstrained DOSD2	High-resolution data Feng and Brion[9]	Low-resolution data Feng and Brion[9]	Jhanwar and Meath[1]
6.082–7.4	1.368(–2)	1.348(–2)	8.936(–3)	1.348(–2)	9.750(–3)
7.4–10.3	4.240(–1)	3.977(–1)	3.882(–1)	3.977(–1)	3.995(–1)
10.3–11.8	5.566(–1)	5.415(–1)	5.334(–1)	5.415(–1)	5.625(–1)
11.8–13.0	6.298(–1)	6.189(–1)	6.062(–1)	6.189(–1)	6.722(–1)
13.0–15.0	1.405	1.372	1.369	1.372	1.471
15.0–17.0	1.545	1.516	1.516	1.516	1.600
17.0–19.0	1.539	1.513	1.522	1.513	1.607
19.0–21.0	1.447	1.423	1.432	1.423	1.516
21.0–24.0	1.843	1.802	1.822	1.802	1.617
24.0–27.0	1.441	1.413	1.439	1.413	1.260
27.0–30.0	1.139	1.120	1.158	1.120	1.005
30.0–32.0	6.321(–1)	6.258(–1)	6.550(–1)	6.258(–1)	5.701(–1)
32.0–35.0	8.148(–1)	8.039(–1)		8.039(–1)	7.302(–1)
35.0–40.0	1.066	1.047		1.047	9.654(–1)
40.0–50.0	1.459	1.421		1.421	1.362
50.0–70.0	1.610	1.561		1.561	2.054
70.0–100.0	1.095	1.071		1.071	1.346
100.0–200.0	1.159	1.131		1.131	1.248
200.0–300.0	6.168(–1)	6.087(–1)			6.087(–1)
300.–500.	2.141	2.050			2.050
500.–700.0	1.395	1.355			1.355
700.–1000.	9.592(–1)	9.400(–1)			9.400(–1)
1000–∞	1.069	1.045			1.045

[a] Numbers in parentheses indicate a power of ten.

27–30 and 30–32 eV. The integrated DOSs obtained from the low resolution DOSs of Feng and Brion[9] (essentially) agree with our recommended results to with the experimental error of ≈5% over the entire wide range of photon energies for which the experimental results are available. The integrated DOSs corresponding to the recommended ethanol DOSD of Jhanwar and Meath[1] often agree with our recommended results to (essentially) within either 5 or 10% with significant exceptions being –29, 28 and 23% for 6.1–7.4, 50–70 and 70–100 eV, respectively. In contradistinction to the result obtained for the high- and low-resolution data, those due to the original[1] ethanol constrained DOSD show discrepancies with respect to our recommended results that vary in sign as E changes and thus, as discussed previously for methanol, these discrepancies tend to cancel when calculating the molecular properties of ethanol. A discussion of other DOS data, and the related integrated DOSs, involved in the construction of the original constrained DODS for ethanol can be found in the literature[1,9].

DIPOLE PROPERTIES

Results for the molar refractivity of methanol calculated from the recommended DOSD are tabulated in Table II, for various wavelengths between 2302 and 6709 Å, where they are compared with the available experimental data of Ramaswamy[33]; for common wavelengths the agreement is excellent as expected from the use of the extremes of the experimental data as constraints in constructing the DOSD. The results for the molar refractivity of ethanol, for 2302 Å ≤ λ ≤ 6709 Å, are listed in Table IV. They usually agree to within 0.001 with the results computed with the recommended DOSD for ethanol developed by Jhanwar and Meath[1] (there are misprints in the refractivity results for ethanol in this paper) with the exceptions being disagreements of 0.003, 0.004, 0.003 and 0.002 between 2753 and 3985 Å. Also included in Table IV are results for the molar refractivity of ethanol calculated using our unconstrained DOSD2 for this molecule. Clearly, the effects of the constraints are significant – the unconstrained results are 2.5% lower than the recommended values. A discussion of refractivity data for propan-1-ol can be found in the original alcohol paper[1].

The results for the methanol dipole properties S_k, $k = –10(2)–4(1)–3(1/2)0, 1, 2$, and the logarithmic dipole sums L_k and mean excitation energies I_k, $k = –2(1)2$, evaluated using both the constrained and unconstrained methanol DOSD2, are compared for common properties, with the literature results of Olney et al.[51] in Table V. Olney et al.[51] have computed the dipole properties by employing the photoabsorption spectrum of Burton et al.[8];

the calculations were based on the high-resolution data, augmented by the low-resolution data as needed. In order to obtain absolute values of the DOSs for methanol, the original experimental data of Burton et al.[8] were normalized using the valence-shell TKR(VTKR) sum rule[52]. Using the normalized data of Burton et al., Olney et al. obtained S_{-2} = 20.79 and then renormalized the distribution of Burton et al. by satisfying the experimental result[53] S_{-2} = 21.62. It is this renormalized distribution that was used to evaluate the dipole properties of methanol listed in Olney et al.[51]. The dipole properties S_k and L_k corresponding to the absolute scale of the original normalized DOS data of Burton et al. can be obtained from those of Olney et al. by multiplying the latter by the factor 0.9616 which is the ratio of the S_{-2} evaluated from the Burton et al. data to that finally used by Olney et al.; the mean excitation energies are unaffected by this normalization procedure.

TABLE IV
Recommended values of the molar refractivity (in $cm^3\ mol^{-1}$) of C_2H_5OH (ideal gas, STP) evaluated using the recommended DOSD2 and a comparison with results obtained using the initial unconstrained DOSD2

λ, Å	Recommended DOSD2	Unconstrained DOSD2
6709	13.0938	12.7674
6440	13.1134[a]	12.7864
5893	13.1624	12.8338
5462	13.2124	12.8822
5087	13.2673	12.9353
4917	13.2967	12.9637
4801	13.3187	12.9850
4603	13.3606	13.0255
4359	13.4209	13.0839
3985	13.5383	13.1974
3342	13.8561	13.5045
2926	14.2104	13.8468
2753	14.4216	14.0507
2302	15.3399[a]	14.9367

[a] Used as constraints in constructing the DOSD.

TABLE V

The dipole sums S_k, logarithmic dipole sums L_k and mean excitation energies I_k for CH_3OH evaluated using the recommended and unconstrained DOSD2 and a comparison with literature results[a]

Property	Unconstrained DOSD2	Recommended DOSD2	Jhanwar and Meath[1]	Olney et.al.[51]
S_2	1.399(4)	1.410(4)	1.397(4)	
S_1	1.474(2)	1.492(2)	1.470(2)	
S_0	1.733(1)	1.800(1)	1.800(1)	
$S_{-0.5}$	1.396(1)	1.461(1)	1.463(1)	
S_{-1}	1.450(1)	1.519(1)	1.518(1)	1.491(1)
$S_{-1.5}$	1.690(1)	1.767(1)	1.764(1)	
S_{-2}	2.107(1)	2.194(1)	2.194(1)	2.162(1)
$S_{-2.5}$	2.760(1)	2.858(1)	2.863(1)	
S_{-3}	3.762(1)	3.874(1)	3.887(1)	3.783(1)
S_{-4}	7.740(1)	7.866(1)	7.891(1)	7.554(1)
S_{-6}	4.557(2)	4.512(2)	4.403(2)	4.071(2)
S_{-8}	3.761(3)	3.652(3)	3.340(3)	2.996(3)
S_{-10}	3.919(4)	3.762(4)	3.159(4)	2.758(4)
L_2	8.887(4)	8.960(4)	8.882(4)	
L_1	4.972(2)	5.015(2)	4.939(2)	
L_0	1.487(2)	1.500(1)	1.481(1)	
L_{-1}	–3.135	–3.252	–3.205	–3.555
L_{-2}	–1.041(1)	–1.064(1)	–1.071(1)	–1.037(1)
I_2, eV	1.565(4)	1.564(4)	1.572(4)	
I_1, eV	7.938(2)	7.840(2)	7.823(2)	
I_0, eV	6.418(1)	6.261(1)	6.194(1)	
I_{-1}, eV	2.192(1)	2.197(1)	2.203(1)	
I_{-2}, eV	1.660(1)	1.676(1)	1.670(1)	

[a] Numbers in parentheses indicate a power of ten.

The results of Olney et al. for the S_k are lower than our recommended values by 1.8, 1.5, 2.3, 3.9, 9.8, 18.1 and 26.7% for $k = -1, -2, -3, -4, -6, -8$ and -10, respectively. For L_{-2} and L_{-1} they are 2.5% higher and 9.3% lower than our results, respectively. Except for S_{-6}, S_{-8} and S_{-10}, the variation between the two sets of results, for common properties, is less than the uncertainties reported in Olney et al.[51]. Results for S_k with $k = -5/2, -3/2, -1/2$, $k \geq 0$, and L_k and I_k with $k \geq 0$, are not available in Olney et al.[51]; those for I_{-2} and I_{-1}, which can be calculated from their corresponding results for the analogous S_k and L_k sums via Eq. (*3*), are 0.5% higher and 2.4% lower than our recommended results. For $k \cong 0$ and $k > 0$, the original DOS data of Burton et al.[8], and hence the DOS results of Olney et al.[51], will lead to poor values for the dipole properties unless extended to higher photon energies and constrained to both refractivity data and the full TRK sum rule $S_0 = 18$. For example, the S_0's evaluated from the unconstrained DOSD1 and DOSD2 are 17.35 and 17.34, respectively; using the Burton et al. data (i.e. up to 360 eV only) yields 14.13 and 14.12, respectively. In order to use the original DOS data in this way requires an extension of those data to very high photon energies as illustrated in the construction of the DOSD*i*, $i = 1, 2$.

Values of the dipole properties evaluated using the original[1] recommended DOSD for methanol are also included in Table V. These results agree to well within 1% with our recommended values of the S_k for $0 \geq k \geq -4$ and $k = 2$, are 2.4, 8.5 and 16% lower than our results for $k = -6, -8$ and -10, respectively, and 1.5% lower for $k = 1$. For the logarithmic dipole sums L_k, the older results are 0.9, 1.5, 1.3 and 0.7% lower than our recommended results for $k = 2, 1, 0$ and -2, respectively, and 1.4% higher for $k = -1$. For the mean excitation energies I_k the original results[1] agree with ours to within 1%.

The results for the dipole properties of ethanol, evaluated using both the constrained and unconstrained DOSD2, are compared with those obtained from the original[1] constrained DOSD in Table VI. The two sets of results are in remarkable agreement for all of the properties. The agreement is usually within 1% with the exceptions being S_2, S_1, S_{-8}, S_{-10}, L_2, L_1 and I_1 where the older results are lower by 2.3, 1.6, 1.6, 3.1, 2.3, 2.1 and 1.8%, respectively.

Also included in Table VI are results for dipole properties of ethanol obtained by Feng and Brion[9]; they were calculated by employing their high-resolution DOS data from the absorption threshold to 32 eV and their low-resolution data from 32 to 200 eV. In order to obtain absolute values of the DOSs, the original experimental data of Feng and Brion were normalized[9] using the valence-shell TKR sum rule[52]. The results of Feng and Brion[9] for common properties are generally significantly different from those ob-

TABLE VI
The dipole sums S_k, logarithmic dipole sums L_k and mean excitation energies I_k for C_2H_5OH evaluated using the recommended and unconstrained DOSD2 and a comparison with literature results[a]

Property	Unconstrained DOSD2	Recommended DOSD2	Jhanwar and Meath[1]	Feng and Brion[9]
S_2	1.725(4)	1.766(4)	1.726(4)	
S_1	1.960(2)	2.012(2)	1.980(2)	
S_0	2.539(1)	2.600(1)	2.600(1)	
$S_{-0.5}$	2.128(1)	2.177(1)	2.171(1)	
S_{-1}	2.264(1)	2.316(1)	2.306(1)	2.236(1)
$S_{-1.5}$	2.674(1)	2.739(1)	2.730(1)	
S_{-2}	3.358(1)	3.443(1)	3.443(1)	3.345(1)
$S_{-2.5}$	4.408(1)	4.528(1)	4.540(1)	
S_{-3}	6.006(1)	6.179(1)	6.209(1)	5.948(1)
S_{-4}	1.223(2)	1.264(2)	1.271(2)	1.203(2)
S_{-6}	6.846(2)	7.126(2)	7.101(2)	6.623(2)
S_{-8}	5.191(3)	5.427(3)	5.338(3)	4.920(3)
S_{-10}	4.914(4)	5.140(4)	4.979(4)	4.549(4)
L_2	1.084(5)	1.109(5)	1.084(5)	
L_1	6.453(2)	6.620(2)	6.478(2)	
L_0	1.933(1)	1.990(1)	1.992(1)	
L_{-1}	–5.702	–5.864	–5.843	–6.521
L_{-2}	–1.690(1)	–1.743(1)	–1.764(1)	–1.670(1)
I_2, eV	1.457(4)	1.454(4)	1.454(4)	
I_1, eV	7.322(2)	7.308(2)	7.176(2)	
I_0, eV	5.822(1)	5.850(1)	5.856(1)	
I_{-1}, eV	2.115(1)	2.113(1)	2.112(1)	
I_{-2}, eV	1.645(1)	1.640(1)	1.630(1)	

[a] Numbers in parentheses indicate a power of ten.

tained originally[1] and those calculated using our recommended DOSD2. Their S_k, for $k = –1, –2, –3, –4, –6, –8$ and $–10$, and $L_{–1}$, are, respectively, 3.5, 2.8, 3.7, 4.8, 7.1, 9.3, 11.5 and 11.2% lower than our recommended results for these properties while their $L_{–2}$ is 4.2% higher than our value. The values of $I_{–1}$ and $I_{–2}$ evaluated by using the Feng and Brion results for the corresponding L_k and S_k via Eq. (*3*) are 3.8% lower and 0.7% higher than our recommended values for these properties.

It should be noted that results for these properties of ethanol obtained by our unconstrained DOSD2 do not, and should not, agree closely with those of Feng and Brion[9]. As discussed earlier our recommended DOSD2, obtained by using the low-resolution DOS data of Feng and Brion from threshold to 200 eV, is preferred relative to the constrained DOSD1 obtained from replacing the low-resolution data by the high-resolution data from threshold to 32 eV. We have calculated the dipole properties of ethanol using our unconstrained DOSD1 which (essentially) corresponds to the Feng and Brion[9] calculations except DOSD1 has DOS data for $E > 200$ eV whereas the calculations in ref.[9] do not. For the dipole sums S_k, $k \leq –1$ considered in ref.[9], contributions from $E > 200$ eV should be small for $k = –1$ to negligible as k decreases[21,40,46,48,49,54,55]. But for the logarithmic dipole sums L_k, this is not the situation for $k = –1$; depending on the molecule, this property can have a long tail regarding the contribution of large photon energies to its defining integral (Eq. (*2*) with $k = –1$)[40]. Thus using DOSD1, we obtain excellent agreement with their results except for $S_{–1}$ and $L_{–1}$ where their values are 1.4 and 16% lower than our DOSD1 results of 22.68 and –5.62. The DOSD1 contributions to $S_{–1}$ and $L_{–1}$ for $E < 200$ eV are 22.35 and –6.52, respectively, while those for $E > 200$ eV are 0.33 and 0.91, respectively. The values for $E < 200$ eV agree precisely with those given by Feng and Brion[9].

The dipole properties of propan-1-ol, and a related discussion, can be found in the original alcohol paper[1].

The results for the dipole properties for methanol and ethanol developed here, and those for propan-1-ol obtained by Jhanwar and Meath[1], are the most reliable compendia of such properties for these alcohols. References to other literature results for some of these properties have been given previously and other relevant literature can be found in these references.

A previous literature discussion[56] of the dipole properties associated with the radiation interactions of alcohols, which is of interest in radiation research, is little changed by the results of the current work. This was based on the results for the original[1] recommended DOSDs and properties for the alcohols. The properties of specific interest are S_k, L_k and I_k, $k = 1, 0, -1$, and the original results of these for methanol and ethanol differ little from our recommended result of this paper. For example, the mean excitation energies I_0 for the stopping of fast charged particles in methanol and ethanol obtained here, namely 62.61 and 58.50 eV, agree very well, to within 1 and 0.1%, with those obtained in the original constrained DOSD work for the alcohols[1]; there is no reason to suppose the result for propan-1-ol obtained earlier[1], 56.82 eV, is not equally reliable. Experimental results[57–59] for I_0, with uncertainties of 3–4%, are available for the liquid alcohols and they are 8, 7.4 and 7.5% higher than our recommended DOSD results for the gas. As has been discussed previously[59–62], the difference between the two sets of average energies is due to two effects: (i) a phase effect and (ii) difficulties associated with the extraction of values for the mean excitation energy from experimental stopping power measurements; these difficulties have been discussed previously[21] and can be avoided by using the constrained DOSD approach for molecules in the gaseous state. There seems to be no doubt that the phase effect causes an increase in I_0 for the liquid relative to the gas[56,59].

DISPERSION ENERGY COEFFICIENTS

The dipolar dispersion energy coefficients are generally most conveniently evaluated by using discrete representations (pseudo-DOSDs) of the recommended constrained DOSDs for the interacting species[10,11]. This representation of the original DOSD of the molecule is particularly useful for the efficient evaluation of the triple-dipole dispersion energy which is given in terms of a triple integral involving the original continuous DOSD of the interacting species[11,12]. The pseudo-DOSD for a given molecule is determined from known values of the dipole sums S_k by requiring

$$S_k = \sum_{i=1}^{n} (E_i / E_{\mathrm{H}})^k f_i \ , \quad k = 2, 1, 0, -1, -2, \ldots, 3-2n \qquad (9)$$

The values of $2n$ dipole sums generate n pseudo-dipole (excitation energy–oscillator strength) pairs (E_i, f_i). The ten pseudo-state representation of the constrained DOSD2 for methanol and ethanol is given in Tables VII and VIII, respectively. They are more than adequate for evaluating the dipole-dipole and the triple-dipole dispersion energy coefficients, for interactions involving the alcohol molecules, to well within the accuracy (≤1% for dipole-dipole, ≤1–2% for triple-dipole) generally expected[10–12] from using

TABLE VII
The values[a] of the pseudo-DOSD excitation energies (in units of E_H) and oscillator strengths for ground-state CH_3OH

E_i	f_i
2.32474(–1)	2.25272(–3)
2.63789(–1)	2.31246(–2)
3.15238(–1)	1.22229(–1)
4.11272(–1)	6.89652(–1)
5.52789(–1)	2.48199
8.13334(–1)	3.97740
1.41789	3.78445
3.42480	2.68819
2.09400(1)	4.06929
2.75737(2)	1.61427(–1)

[a] Numbers in parentheses indicate a power of ten.

TABLE VIII
The values[a] of the pseudo-DOSD excitation energies (in units of E_H) and oscillator strengths for ground-state C_2H_5OH

E_i	f_i
2.30797(–1)	2.22111(–3)
2.65271(–1)	2.66211(–2)
3.19369(–1)	2.26866(–1)
4.07457(–1)	1.15171
5.51170(–1)	3.75699
8.04986(–1)	6.10020
1.38831	5.31925
3.36615	3.35090
2.01450(1)	5.85102
2.66661(2)	2.14210(–1)

[a] Numbers in parentheses indicate a power of ten.

the original constrained DOSD. We have also computed the pseudo-DOSD for propan-1-ol using the S_k determined from the recommended DOSD for the molecule constructed by Jhanwar and Meath[1] (Table IX).

The results for the C_6 coefficients, obtained using the pseudo-state analogue of Eq. (*5*) which is readily available in the literature[10,16], for the interaction of methanol, ethanol and propan-1-ol with themselves and with some thirty-six other atoms and molecules, can be found (units of $E_H a_0^6$) in Tables X–XII, respectively. In these calculations the alcohol molecules are represented by the pseudo-states listed in Tables VII–IX and the pseudo-states for the other species can be found in the literature[6,7,10,12,41,45–48,50,63–66]. The uncertainties are ≈1%.

The pseudo-state expression for the triple-dipole dispersion energy coefficient C_9 can be found in the literature[11]. Using the pseudo-states given in Tables VII–IX, the triple-dipole dispersion energy coefficients C_9 for the interaction of any three alcohols taken from methanol, ethanol and propan-1-ol can be evaluated with an estimated error of less than 2%. The results are given, in units of $E_H a_0^9$, in Table XIII. The C_9 coefficients for all the interactions involving the alcohols and any of the other species occurring in the earlier tables can be evaluated by using the pseudo-states for the species referred to previously.

TABLE IX
The values[a] of the pseudo-DOSD excitation energies (in units of E_H) and oscillator strengths for ground-state n-C_3H_7OH

E_i	f_i
2.36503(–1)	2.73467(–3)
2.74970(–1)	4.28587(–2)
3.28975(–1)	4.20851(–1)
4.15410(–1)	1.71096
5.59623(–1)	5.39148
8.07092(–1)	7.64478
1.43248	6.35278
3.32963	4.72380
1.95945(1)	7.45022
2.60527(2)	2.59515

[a] Numbers in parentheses indicate a power of ten.

TABLE X
Recommended values for the dipole-dipole dispersion energy coefficients $C_6(CH_3OH, B)$ for the interaction of CH_3OH with various species B (in units of $E_H a_0^6$)

B	$C_6(CH_3OH, B)$	B	$C_6(CH_3OH, B)$	B	$C_6(CH_3OH, B)$
CH_3OH	222.0	HCl	170.0	SiF_4	266.9
H	37.23	HBr	218.4	CCl_4	669.4
Li	338.5	CO	134.3	C_2H_2	212.2
He	17.56	CO_2	187.3	C_6H_6	616.5
Ne	35.79	NO	124.0	NH_3	140.6
Ar	119.3	N_2O	202.4	CH_3NH_2	259.5
Kr	169.6	H_2O	100.2	$(CH_3)_2NH$	379.0
Xe	251.1	SO_2	255.4	$(CH_3)_3N$	485.5
H_2	51.63	CS_2	431.0	CH_2O	191.5
N_2	127.3	COS	297.0	CH_3CHO	298.6
O_2	116.2	H_2S	217.4	$(CH_3)_2CO$	419.8
Cl_2	293.4	SF_6	352.3		
HF	64.19	SiH_4	272.5		

TABLE XI
Recommended values for the dipole-dipole dispersion energy coefficients $C_6(C_2H_5OH, B)$ for the interaction of C_2H_5OH with various species B (in units of $E_H a_0^6$)

B	$C_6(C_2H_5OH, B)$	B	$C_6(C_2H_5OH, B)$	B	$C_6(C_2H_5OH, B)$
C_2H_5OH	535.2	HCl	264.1	SiF_4	413.5
H	57.94	HBr	339.5	CCl_4	1040
Li	530.1	CO	208.5	C_2H_2	329.8
He	27.20	CO_2	290.6	C_6H_6	958.0
Ne	55.35	NO	192.4	NH_3	218.5
Ar	185.2	N_2O	314.2	CH_3NH_2	403.1
Kr	263.3	H_2O	155.4	$(CH_3)_2NH$	588.7
Xe	390.2	SO_2	396.5	$(CH_3)_3N$	754.2
H_2	80.26	CS_2	670.6	CH_2O	297.4
N_2	197.5	COS	461.8	CH_3CHO	463.7
O_2	180.2	H_2S	338.1	$(CH_3)_2CO$	652.0
Cl_2	455.9	SF_6	545.8	CH_3OH	344.6
HF	99.48	SiH_4	423.9		

TABLE XII
Recommended values for the dipole-dipole dispersion energy coefficients $C_6(C_3H_7OH, B)$ for the interaction of n-C_3H_7OH with various species B (in units of $E_H a_0^6$)

B	$C_6(C_3H_7OH, B)$	B	$C_6(C_3H_7OH, B)$	B	$C_6(C_3H_7OH, B)$
C_3H_7OH	973.8	HCl	356.3	SiF_4	556.7
H	78.31	HBr	458.2	CCl_4	1403
Li	720.7	CO	281.1	C_2H_2	445.1
He	36.59	CO_2	391.6	C_6H_6	1293
Ne	74.40	NO	259.2	NH_3	294.7
Ar	249.6	N_2O	423.6	CH_3NH_2	543.8
Kr	355.1	H_2O	209.5	$(CH_3)_2NH$	794.2
Xe	526.6	SO_2	534.7	$(CH_3)_3N$	1017
H_2	108.3	CS_2	906.3	CH_2O	401.1
N_2	266.2	COS	623.4	CH_3CHO	625.4
O_2	242.7	H_2S	456.7	$(CH_3)_2CO$	879.4
Cl_2	615.3	SF_6	734.8	CH_3OH	464.8
HF	134.0	SiH_4	572.7	C_2H_5OH	721.9

TABLE XIII
Recommended values for the triple-dipole dispersion energy coefficients for all three-body interactions involving A = CH_3OH, B = C_2H_5OH and C = n-C_3H_7OH molecules (in units of $E_H a_0^9$)

Interaction	C_9	Interaction	C_9
A–A–A	3498.6	B–B–A	85 099
A–A–B	5456.3	B–B–C	17 972
A–A–C	7386.8	C–C–C	32 953
A–B–C	11 522	C–C–A	15 600
B–B–B	13 273	C–C–B	24 335

Spackman[67] has carried out time-dependent Hartree–Fock (TDHF) calculations for C_6 and C_9, for the dimers and trimers, respectively, of methanol, ethanol and propan-1-ol using a 6-31G(+ sd + sp) basis set. His results of 180.6, 449.7, 835.5 and 2526.5, 10048, 25573, respectively, are 18, 16, 14 and 28, 24, 22% lower than our recommended results. As thoroughly discussed by Spackman[67–69], who has used many of our previous constrained DOSD results for C_6 and C_9 for a variety of molecules to assess the situation, this level of TDHF calculation cannot be expected to give accurate results for these dispersion energy coefficients.

Spackman has discussed the systematics of the deviations of 6-31G(+ sd + sp) TDHF results of the dispersion energy coefficients from the constrained DOSD values and has shown how to correct the TDHF results to obtain values much closer to the DOSD results if the static dipole polarizabilities of the interacting species are known both at the 6-31G(+ sd + sp) TDHF level of approximation and reliably (for example experimentally or through a constrained DOSD analysis). His equations for the predicted values have the form

$$C_{6,\mathrm{pre}} = c[\alpha_{d,\exp} / \alpha_{d,\mathrm{TDHF}}]^a C_{6,\mathrm{TDHF}} \qquad (10)$$

and

$$C_{9,\mathrm{pre}} = d[\alpha_{d,\exp} / \alpha_{d,\mathrm{TDHF}}]^b C_{9,\mathrm{TDHF}} \qquad (11)$$

where in Spackman's work the parameters a, b, c and d are $a = 2$, $b = 3$, $c = 0.9435$ and $d = 0.9283$. Using Spackman's results[68] for $\alpha_{d,\mathrm{TDHF}}$, $C_{6,\mathrm{TDHF}}$ and $C_{9,\mathrm{TDHF}}$ and our recommended values of S_{-2} as $\alpha_{d,\exp}$, one obtains $C_{6,\mathrm{pre}}$ = 223.3, 537.0 and 988.2, and $C_{9,\mathrm{pre}}$ = 3519.4, 13284 and 33321 for the like interactions involving methanol, ethanol and propan-1-ol, respectively; these results differ with our recommended results by only 0.6, 0.3 and 1.5, and 0.6, 0.1 and 1.1%, respectively.

More recently Cybulski and Haley[70] have discussed several new approximations for calculating the dispersion energy coefficients C_6 and C_9 based on Eqs (*10*) and (*11*) for the interactions of like species. They develop several schemes using our literature DOSD results to determine the parameters and test their results against our accurate DOSD results for some fourteen interactions involving rare gases, HF, N_2, CO, H_2O, and normal alkanes. Three schemes are of particular relevance to the present work. These approximations for C_6 are based on Eq. (*10*) with $a = 2$ and $c = 0.9515$ (scheme A2), $a = 1$and $c = 1$ (scheme A3), $a = 1.12$ and $c = 1$ (scheme A4); against the test DOSD data the standard deviations of the approximate results[70] are 2.4, 1.2 and 0.7%, respectively. For C_9 the approximations are based on Eq. (*11*) with $b = 3$ and $d = 0.9459$ (scheme B2), $b = 3/2$ and $d = 1$ (scheme B3), $b = 2.022$ and $d = 1$ (scheme B4); against the test DOSD data the standard deviations of the approximate results[70] are 2.6, 3.7 and 1.0%, respectively.

At the suggestion of reviewers we have calculated approximations for the dispersion energy coefficients for the like alcohol interactions involving methanol, ethanol and propan-1-ol using the above schemes. The TDHF polarizabilities, C_6 and C_9 values are taken from Spackman[67,68] (they are not available in ref.[70]). For C_6, the average deviations of the results obtained from schemes A2–A4 with respect to our recommended DOSD results for the like alcohol interactions are 1.6, –5.4 and –4.0%, respectively. The analogous average deviations for the C_9 coefficients are 2.5, –9.8 and –3.8%. These estimates are inferior to those obtained by using the Spackman's approach (see above). The reason is probably due to the fact that Spackman's scheme is tailor made for the use of 6-31G(+ sd + sp) TDHF results for the input polarizabilities and dispersion energy coefficients whereas the schemes of Cybulski and Haley[70] have been set up using higher level basis set values for the input TDHF quantities; the TDHF input from refs[67,68] and ref.[70], are significantly different. In any case the discussion in ref.[70] contains interesting discussions concerning *ab initio* and DFT calculations of dispersion energies.

DISCUSSION AND CONCLUSIONS

Estimates for the uncertainties in our recommended values for molecular dipole properties, evaluated using the constrained dipole oscillator distribution approach, are based on a method developed and used previously[2,6,7,21,40]. Namely the recommended results are compared with those obtained from alternative DOSDs satisfying the same constraints (i.e., DOSD1 and DOSD2 for methanol and ethanol in this paper and the various DOSDs considered for all three alcohols in ref.[1]). For the properties that depend significantly[21,40,49,54,55] on energy regions of the DOSD that dominate the constraints used in constructing the DOSDs, that is the S_k, L_k and I_k for $-6 \leq k \leq 2$, the estimated errors are ≤1–2%. The uncertainties will increase, relatively slowly, as k decreases for $k < -6$ because local errors in the DOSD for small photon energies are magnified for these properties[21,10,49,54,55]; they can be as high as 10 to 15% for S_{-10}. These error estimates assume reliable values (errors of a few tenths of a per cent) for the molar refractivities used as constraints. While this is almost certainly true for methanol, it does rely on the reliability of the additivity of the refractivity for ethanol and propan-1-ol relative to methanol for the other two alcohols[1].

As indicated earlier, part of motivation for this work was to verify the reliability of the results for the dipole properties of the alcohols obtained in the original[1] constrained DOSD analysis for these molecules. That work was carried out in the early 1980's and was based on the then available DOS data for the molecules which, as discussed earlier in the present paper, were sparse, from various experimental groups, with no direct experimental DOS data being available for photon energies greater than 100 eV (in ref.[1] the higher energy DOSs were obtained via mixture rules). Also there was a gap in the available data for methanol between 21 and 30 eV, a region of photon energies of importance for properties related to molar refractivities (e.g. polarizabilities and van der Waals coefficients). The constrained DOSD analysis in the current paper for methanol and ethanol, which is based on extensive experimental DOS data from a single experimental group[8,9], indicates that the results for the properties of these molecules obtained originally are indeed reliable and that the present recommended values offer only a marginal improvement, mostly for $k \leq -6$. Similarly, the values of the dipole properties of methanol and ethanol for $k \leq 1$ obtained by Olney et al.[51] and Feng and Brion[9], which were obtained in 1992 and 2002 by using the same experimental molecular DOS data base as used in the present paper (with no extension beyond 360 and 200 eV using mixture rules) and an energy-independent normalization approach, offer little improvement relative to the original[1] evaluation of these properties. This indicates the power of the constraint procedure used in our work, namely the reproduction of experimental molar refractivity data and the satisfaction of the full Thomas–Reiche–Kuhn sum rule ($S_0 = N$). The use of both of these constraints normalizes the complete DOSD, from small to very large E, in a smooth and continuous and energy-dependent manner. Energy-independent normalization[9,51] and/or no extension of the DOS data base to very high photon energies can lead to difficulties in determining reliable values of atomic and molecular dipole properties even from extensive experimental DOS data sets; this has been discussed in the literature (see, for example, refs[46,48] and some of the citations therein) and is also illustrated by the discussion of the dipole properties of methanol and ethanol given earlier here.

On the other hand, the results for the integrated dipole oscillator strengths corresponding to our recommended DOSDs for methanol and ethanol are probably more reliable than those of Jhanwar and Meath[1]. For example the standard deviations (STDs) for our recommended DOSDs for these molecules are 3.96 and 1.16 vs 7.52 and 2.70 for the original[1] recommended DOSDs; the STD for the recommended[1] DOSD for propan-1-ol is 2.75. The lower the STD, the less modification of the input DOS data is required in order to satisfy the constraints imposed on the recommended DOSDs; the change in the STDs for the methanol DOSDs is significant. See also the discussions in Jhanwar and Meath[1] of DOSs for all three alcohols, and in Burton et al.[8] and Feng and Brion[9] of DOSs for methanol and ethanol, respectively; these papers include a comparison of their results with various literature DOSs including in ref.[8] those obtained from the constrained methanol DOSD of Jhanwar and Meath[1].

The results for the dipole-dipole and the triple-dipole dispersion energies for the interactions considered in this paper are new and are apparently the only reliable values available for these molecules. They represent prototype interactions involving prototypical molecules containing the alcohol group and therefore should be of considerable interest. The estimated errors for the C_6 and C_9 results given in this paper are 1 and 2%, respectively, with the caveat that the error estimates depend on the reliability of the molar refractivity constraints used in the construction of the alcohol DOSDs as discussed previously.

The importance of these dispersion energies has been addressed in a general manner earlier in this paper. A relatively recent specific example is provided by the work of Buck et al.[71] who developed a potential energy surface for methanol–methanol interactions in order to help discuss the structure and vibrational spectra of methanol clusters. In developing the dispersive part of the surface they show how to use the constrained isotropic DOSD results for the dipole-dipole dispersion energy coefficients for the methanol–methanol[72], methane–methane[10] and water–water[15] interactions to obtain anisotropic methanol–methanol dispersion energy results through the construction of separate C_6(C–C), C_6(O–O) and C_6(C–O) coefficients for the C and O "atoms" in the methanol molecule.

Accurate DOSD values of C_6 for important prototype interactions furnish useful checks of other methods for evaluating dispersion energy coefficients, for example empirical, non-empirical, *ab initio* quantum mechanical, and Padé approximant approaches[10,11,15,28,29,50,67,73–78]. In this context it is relevant to point out that in the construction of potential energy models[24–30] (mentioned briefly previously), it is necessary to include the dispersion energy to at least terms that vary as R^{-10} at long range. The terms varying as powers of R^{-1} higher than R^{-6} are not accessible by DOSD techniques due to the lack of (experimental) higher multipole (than dipole) oscillator strengths. The method of choice for determining these higher-order dispersion energies is via *ab initio* quantum mechanical methods analogous to those used for the dipole-dipole case. The reliability of these methods for these energies can be checked indirectly via the checks on the dipole-dipole dispersion energy referred to earlier since the *ab initio* calculation of the higher-order terms is not easier than for the dipole-dipole dispersion energy. In any event, as pointed out earlier, the dipole-dipole dispersion energy is the lead or dominant dispersion energy and the success of the potential energy models depends[26,55] on a reliable value of the coefficient C_6.

The pseudo-DOSDs employed in this work to calculate the dipole-dipole and the triple-dipole dispersion energy coefficients form a concise representation of the original recommended DOSDs for the alcohol molecules, which are continuous functions of the excitation energy from the UV absorption threshold to many thousands of eV. They give reliable results for the dispersion energy coefficients and a variety of other molecular properties through the use of discretized analogues of the usual expressions for these properties[10–12]. We emphasize that more than ten pseudo-states[79] are needed to reliably evaluate some of these properties, for example the logarithmic dipole sums L_k for "larger" values of k, which have significant negative and positive contributions[40,48,66].

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