Dipole oscillator strength distributions, sum rules, mean excitation energies, and isotropic van der Waals coefficients for benzene, pyridazine, pyrimidine, pyrazine, s-triazine, toluene, hexafluorobenzene, and nitrobenzene

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Experimental, theoretical, and additive-model photoabsorption cross-sections combined with constraints provided by the Kuhn-Reiche-Thomas sum rule and the high-energy behavior of the dipole-oscillator-strength density are used to construct dipole oscillator strength distributions for benzene, pyridazine (1,2-diazine), pyrimidine (1,3-diazine), pyrazine (1,4-diazine), s-triazine (1,3,5-triazine), toluene (methylbenzene), hexafluorobenzene, and nitrobenzene. The distributions are used to predict dipole sum rules $S(k)$ for $-6 \leq k \leq 2$, mean excitation energies $I(k)$ for $-2 \leq k \leq 2$, and isotropic van der Waals $C_6$ coefficients. A popular combination rule for estimating $C_6$ coefficients for unlike interactions from the $C_6$ coefficients of the like interactions is found to be accurate to better than 1% for 606 of 628 cases (96.4%) in the test set.

I. INTRODUCTION

The current interest in non-covalent interactions has generated renewed efforts to develop improved theoretical methods for the calculation of van der Waals interactions. It is important to have reliable, experiment-based, reference values of the van der Waals dispersion coefficients $C_6$ to assess these theoretical methods. Since the early insight of Margenau,\textsuperscript{2} the most reliable experiment-based values of $C_6$ coefficients have been obtained from dipole oscillator strength distributions (DOSDs). The DOSD of an atom or molecule consists of the set of discrete excitation energies $E_i$ and oscillator strengths $f_i$ together with the differential dipole oscillator strength (DOS) function $(df/dE)$ for the continuum of energies $E_c \leq E < \infty$ that begins at the continuum threshold $E_c$. The DOS is proportional to the photo-absorption cross section, $\sigma$. Many constructions of a complete DOSD from experimental data possibly subject to a few constraints have been reported; for a representative sample, see Refs.\textsuperscript{4,8}

No complete DOSDs are available for (hetero)aromatic molecules apart from benzene\textsuperscript{2} and pyridine.\textsuperscript{2} The purpose of this work is to report the construction of constrained DOSDs and the resulting dipole sum rules $S(k)$ for $-6 \leq k \leq 2$, mean excitation energies $I(k)$ for $-2 \leq k \leq 2$, and isotropic van der Waals $C_6$ coefficients for pyridazine (1,2-diazine), $\text{C}_6\text{H}_4\text{N}_2$, pyrimidine (1,3-diazine), $\text{C}_6\text{H}_4\text{N}_2$, pyrazine (1,4-diazine), $\text{C}_6\text{H}_4\text{N}_2$, s-triazine (1,3,5-triazine), $\text{C}_6\text{H}_4\text{N}_2$, toluene (methylbenzene), $\text{C}_6\text{H}_5\text{CH}_3$, hexafluorobenzene ($\text{C}_6\text{F}_6$), and nitrobenzene ($\text{C}_6\text{H}_4\text{NO}_2$). Moreover, an improved DOSD is reported for benzene ($\text{C}_6\text{H}_6$) because the available DOSD\textsuperscript{2} is now 28 years old and much new experimental photoabsorption data has become available since then.

This work is organized as follows. Section II is a summary of the experimental data, additive models, and methods used to construct the DOSDs. Section III contains a discussion of the resulting DOSDs and molecular properties. Section IV contains some thoughts about the future of DOSD constructions.

II. METHODS AND DATA

A. Experimental data

Photoabsorption measurements for benzene\textsuperscript{10,15} more recent than the 1992 DOSD construction\textsuperscript{2} are available over the extended energy range from 3.76 eV to 200 eV. Experimental photoabsorption data is available for the other molecules only over a smaller energy range, roughly 4 eV to 40 eV. Fortunately, this energy range accounts for 90% or more of the polarizability.\textsuperscript{16,17} Experimental photoabsorption cross-sections are available from 4.4 eV to 40 eV for pyridazine (1,2-diazine)\textsuperscript{25} from 3.6 eV to 40 eV for pyrimidine (1,3-diazine)\textsuperscript{19–21} from 4.5 eV to 40 eV for pyrazine (1,4-diazine)\textsuperscript{19–21} from 3.9 eV to 39 eV for s-triazine (1,3,5-triazine)\textsuperscript{19–22} from 3.9 eV to 35.6 eV for toluene\textsuperscript{23–30} and from 4.2 eV to 41.3 eV for hexafluorobenzene\textsuperscript{31–33} For nitrobenzene, experimental photoabsorption data is available\textsuperscript{34–36} for most of the energy range from 3.3 eV to 35.6 eV but there is a gap from 8.1 eV to 9.9 eV. This gap was filled by forward extrapolation of Nagakura et al.’s data\textsuperscript{37} and backward extrapolation of Cooper et al.’s data\textsuperscript{38} to their intersection point at roughly 8.4 eV. Digital files of most of the data mentioned in this paragraph were obtained either from the MPI-Mainz UV/VIS Spectral Atlas\textsuperscript{37} or the Brion laboratory’s database.\textsuperscript{38}

Gas-phase measurements of the molar refractivity can be used as constraints for the constructed DOSDs. However, they are available for only one of the eight molecules considered in this work: benzene.\textsuperscript{39,40}
B. Additive models

Photoabsorption data is unavailable at higher energies: $E > 200$ eV for benzene, $E > 35$ eV for toluene and nitrobenzene, and $E > 40$ eV for the five other molecules. Additive models are used to approximate this higher energy data.

The simplest additive models are based on free-atom cross-sections, $\sigma$, were constructed from each of two free-atom additive models. One model, hereafter referred to as $A(C)$, is based on free-atom cross-sections taken from the semiempirical compilation of Henke et al. that extends to 30,000 eV. The other model, hereafter referred to as $A(C)$, is based on free-atom cross-sections tabulated by Chantler for energies up to 100,000 eV. Atom-additive models are expected to be sufficiently accurate for $E > 70$ eV but have been used, in favorable circumstances, for energies as low as 15 eV.

More elaborate and presumably more accurate additive models can be constructed from molecular fragments (groups) provided that consistent data obtained by the same experimental technique and preferably from the same laboratory is available. Photoabsorption cross-sections, in the region from 25 eV to 200 eV, were generated from two fragment-additive models for all the molecules except benzene. The accuracy of a fragment-additive model depends partly on the choice of the fragments. Chemical intuition can be used to help choose the fragments. For example, the conceptual partition of the target species into fragments should minimize disruption of rings and functional groups.

Since all the molecules studied in this work are closely related to benzene, it makes sense to use benzene as one of the fragments and construct an appropriate correction term from other fragments. Thus we express the cross-section $\sigma(M)$ for molecule M as

$$\sigma(M) = \sigma(\text{benzene}) + \Delta(M)$$  \hspace{1cm} (1)

The azines are the most straightforward; bond additivity works reasonably well for their polarizabilities. Azines differ from benzene by $m = 1, 2, \ldots$ aza-substitutions, that is substitutions of C–H by N. Fortunately, experimental cross-sections in the desired energy range are available for both benzene and pyridine, the simplest azine ($m = 1$). The most chemically appealing fragment-additive model used for the $m$-azines is

$$\Delta(m\text{-azine}) = m[\sigma(\text{pyridine}) - \sigma(\text{benzene})]$$  \hspace{1cm} (2)

which is exact for benzene ($m = 0$) and pyridine ($m = 1$) and should be reasonably accurate for the diazines ($m = 2$) and triazines ($m = 3$). Another fragment-additive model considered for the azines is given by

$$\Delta(m\text{-azine}) = \frac{m}{2}[\sigma(N_2) - \sigma(C_2H_2)].$$  \hspace{1cm} (3)

The available data limits the accessible fragment models for the other three molecules. One fragment-additive model for hexafluorobenzene is

$$\Delta(C_6F_6) = 6[\sigma(CH_3F) - \sigma(CH_4)]$$  \hspace{1cm} (4)

and another one is

$$\Delta(C_6F_6) = \frac{3}{2}[\sigma(CF_4) - \sigma(CH_4)].$$  \hspace{1cm} (5)

For toluene, the two fragment models considered are

$$\Delta(\text{toluene}) = \sigma(\text{propanone}) - \sigma(\text{ethanal})$$  \hspace{1cm} (6)

and

$$\Delta(\text{toluene}) = \sigma(\text{C}_2\text{H}_6) - \sigma(\text{CH}_4).$$  \hspace{1cm} (7)

One fragment model used for nitrobenzene is

$$\Delta(\text{nitrobenzene}) = \frac{1}{2}\sigma(\text{C}_2\text{H}_6) - \sigma(\text{CH}_4) + \sigma(\text{NO}_2).$$  \hspace{1cm} (8)

A fragment model based on a correction to pyridine rather than benzene is also used for nitrobenzene:

$$\sigma(\text{nitrobenzene}) = \sigma(\text{pyridine}) + \sigma(\text{CO}_2).$$  \hspace{1cm} (9)

For the sake of brevity, the fragment-additive model of Eq. (m) is referred to as $F(m)$.

In this work, all the photoabsorption data used for fragment-additive models was taken exclusively from the Brion database which contains data for 64 species. The data relevant to this work are unpublished data for propanone and ethanal, and published data for benzene, pyridine, nitrogen, ethyne, methyl fluoride, nitrogen dioxide, tetrafluoromethane, and methane and ethane.

C. DOSD construction

A robust method for constructing a DOSD from photoabsorption cross-sections combined with constraints provided by the Kuhn-Reiche-Thomas (KRT) sum rule and usually molar refractivity data was developed and refined, and applied to more than 50 species by Meath and coworkers as traced in Ref. More recently, the method was augmented by a high-energy constraint based on the asymptotic behavior of the DOS. At first, this technique was restricted to homonuclear molecules but it was later generalized to apply to all molecules. Since the initial application of the general method to pyridine it has been applied to 20 more molecules.

A terse summary of this method suffices because a detailed description is available elsewhere. The available photoabsorption data is divided into energy intervals $[E_i, E_{i+1}]$ for $i = 1, \ldots, N$ in which $E_1$ is the absorption threshold, $E_N$ is the highest energy for which a value of the DOS is available, and $E_{N+1} = \infty$. Then a representative selection is made from the initial distributions that can be constructed using different combinations of
experimental photoabsorption data from diverse sources, additive models, constraints, and a three-term Laurent expansion for the asymptotic region $E > E_N$. The KRT sum rule and the high-energy asymptotic behavior are always used as constraints. Initial values of three parameters that appear in the high-energy constraint are obtained from Hartree-Fock values of the electron density at the nucleus, $\rho(0)$, for each of the atoms in the molecule. Gas-phase molar refractivity values were used as low-energy constraints in some of the distributions for benzene. For each selected distribution, iterations of a constrained least-squares procedure are required to determine simultaneously two parameters in the high-energy constraint and the scale factors $1 + a_i$, $i = 1, \ldots, N$ for all the energy intervals. Finally, the best DOSD has to be selected. Uniformity of the scale factors is a reflection of the consistency of the initial data and so the distributions that lead to the smallest standard deviations $s$ of the scaling parameters are considered the best. Almost invariably, several DOSDs lead to values of $s$ very close to the lowest value, and then the distribution leading to the smoothest DOS is selected from among these.

D. Property calculations

Once a final DOSD has been selected, quadrature is used to compute the dipole sums $S(k)$ from

$$S(k) = \int_{E_c}^{\infty} dE \left( \frac{df}{dE} \right) E^k,$$

the logarithmic sums $L(k)$ from

$$L(k) = \int_{E_c}^{\infty} dE \left( \frac{df}{dE} \right) E^k \ln E,$$

and the mean excitation energies from:

$$I(k) = \exp(d \ln S(k)/dk) = \exp(L(k)/S(k)).$$

Atomic units are used in the above and following equations. The expression used for the isotropic dipole polarizability $\alpha(\omega)$ at selected frequencies $\omega$ is:

$$\alpha(\omega) = \int_{E_c}^{\infty} dE \frac{(df/dE)}{E^2 - \omega^2}.$$

Pseudospectral representations of $\{\epsilon_i, f_i, i = 1, \ldots, 10\}$, of the DOSD are generated from the moments $S(k)$, $-17 \leq k \leq +2$. The pseudospectra are used to compute the $C_6$ coefficient for long-range interactions between molecules A and B from the venerable expression

$$C_6(A–B) = \frac{3}{\pi} \int_0^{\infty} \alpha_A(iy)\alpha_B(iy) dy$$

in which $i = \sqrt{-1}$.

III. RESULTS AND DISCUSSION

A. How good are the additive models?

Two atom-additive models A(H) and A(C), two applicable fragment-additive models, and experimentally measured cross-sections are compared with one another for pyridazine, s-triazine, hexafluorobenzene, toluene, and nitrobenzene in Figs. 1, 2, 3, 4, and 5, respectively.

The figures lead to five general observations.

1. The fragment-additive models $F(m)$ are seen to be reasonably accurate at the lower energies where direct measurements are available. Hence the fragment models $F(m)$ are very likely to be adequate for the somewhat higher energy range $35 \text{ eV} \leq E \leq 200 \text{ eV}$ in which they are used in this work.
2. Where direct measurements are available, the fragment-additive models \( F(m) \) are noticeably more accurate than both the atom-additive models \( A(H) \) and \( A(C) \) except for hexafluorobenzene where \( A(H) \) is comparable to \( F(4) \) down to about 30 eV.

3. As noted by Au et al., chemical intuition is not always helpful in predicting which fragment model is more accurate. For example, \( F(3) \) is more accurate than \( F(2) \) even though one might expect \( F(3) \) to be less accurate because the triple bonds in the nitrogen and ethyne molecules are unrepresentative of the bonding in the aromatic ring.

4. The \( A(H) \) model is consistently better than \( A(C) \) especially at lower energies, perhaps because the free-atom data used in \( A(C) \) are based on the Hartree-Fock approximation which neglects electronic correlation.

5. The \( A(H) \) model begins to converge to the fragment models at energies larger than about 65 eV. It can be used with confidence for \( E > 200 \) eV where the Brion data and hence our fragment models end.

B. DOSDs

DOSDs for the eight (hetero)aromatic molecules were obtained with the methods and data described in Sec. II. The number of distributions examined ranged from 14 for pyridazine for which all the available experimental data comes from a single source to 112 for benzene for which there is ample data. The standard deviation \( s \) of the scale factors measures the consistency of the initial data and gives a rough idea of the accuracy of the DOSD. By this indicator, the benzene DOSD is the most accurate; the value of \( 100s = 0.5 \) obtained for benzene in this work is less than a quarter of the value \( 100s = 2.2 \) found for the benzene DOSD constructed decades earlier. Interestingly, unlike the older one, the best benzene DOSD of this work does not include any refractivity constraints. The DOSD for pyrazine is the least accurate \( (100s=3.1) \) and the values of \( 100s \) for the other six molecules are 1.2, 1.3, 1.5, 1.8, 1.8, and 2.2 for toluene, nitrobenzene, s-triazine, pyridazine, hexafluorobenzene, and pyrimidine, respectively. The integrated properties of the DOSDs are expected to be more accurate than the point-wise distributions.

C. Polarizabilities and refractivities

The DOSD polarizabilities \( \alpha(\omega) \) for smaller frequencies are expected to have errors no larger than \( \pm 1\% \) for benzene, \( \pm 3\% \) for pyrazine, and \( \pm 2\% \) for the remaining six molecules. Of the properties mentioned in Sec. II, the one studied the most is the static polarizability \( \alpha(0) \)
usually denoted simply as \( \alpha \). Consider benzene first. The current DOSD value of \( S(-2) = \alpha = 68.19 \) au is 0.6% larger than and supersedes both the older DOSD values\(^a\) and identical recommended value\(^6\) of 67.79 au. Table I compares the values of \( \alpha \) obtained in this work with prior theoretical computations. The density functional theory (DFT) result from the global hybrid functional B3LYP is 1.6% larger than the DOSD value whereas the \( \alpha \) computed with the range-separated hybrid functional \( \omega \text{B97X-D} \) is within 0.1% of the DOSD value. The \textit{ab initio} value obtained\(^c\) with the CC3 coupled-cluster method is just 0.4% too large for benzene.

Now consider trends for the eight molecules. As expected\(^d\), the B3LYP polarizabilities are consistently larger than all the other values. Somewhat unexpectedly, the \( \omega \text{B97X-D} \) are consistently closer to the DOSD values than the CC3 values and the diazines. The largest discrepancies, 3% for CC3 and 2% for \( \omega \text{B97X-D} \), occur for pyrazine whose DOSD is more poorly determined than the DOSDs for the other molecules. Comparison of the DOSD polarizabilities with their free-atom additive model counterparts, based on the exact\(^e\) polarizability for H and accurate coupled-cluster values for the C, N, O, and F atoms\(^f\), shows that all eight molecules satisfy the minimum polarizability principle\(^g\) as more than 97% of all molecules do\(^2\).

Next, turn to the frequency-dependent polarizability \( \alpha(\omega) \) and to the related molar refractivity \( R(\omega) \) given by

\[
R(\omega) = \frac{4\pi\alpha_0^3}{3} N_A \alpha(\omega)
\]

in which \( N_A \) is Avogadro’s constant and \( \alpha_0 \) is the Bohr radius. Table II lists the molar refractivities predicted by the benzene DOSD are about 0.1% larger than the measured values\(^4\) at all five wave lengths. This close agreement comes about even though the best DOSD does not have a refractivity constraint. The small discrepancies of 0.1% imply that there is a small incompatibility between the refractivity data\(^4\) and the low energy photoabsorption cross-sections\(^10\) for benzene. There are no measured gas-phase refractivities for the other seven molecules.

Table III lists \( \alpha(\omega) \) predicted by the DOSDs at two wave lengths and compares them with CC3 values where available\(^8\). Observe that the CC3 values are consistently larger than the DOSD values at both wave lengths. The CC3 and DOSD values differ by only 0.5%, 3%, 2%, and 3% for benzene, pyridazine, pyrimidine, and pyrazine respectively. These discrepancies are within the uncertainty of the DOSD polarizabilities except for pyridazine.

### Table I. Static electronic dipole polarizabilities \( \alpha \) (in au). Multiply by 0.1481847 to get the polarizability volume in \( \text{Å}^3 \).

| Molecule            | B3LYP\(^a\) | \( \omega \text{B97X-D}\)\(^b\) | \textit{Ab initio} | DOSD\(^f\) |
|---------------------|-------------|-------------------------------|------------------|-------------|
| Benzene             | 69.31       | 68.26                         | 68.49\(^f\)      | 68.19\(^f\) |
| Pyridazine          | 58.93       | 58.00                         | 58.73\(^f\)      | 57.09       |
| Pyrimidine          | 58.23       | 57.32                         | 57.81\(^f\)      | 57.00       |
| Pyrazine            | 59.16       | 58.23                         | 58.83\(^f\)      | 57.10       |
| s-Triazine          | 52.42       | 51.67                         | 52.76\(^f\)      | 52.17       |
| Toluene             | 82.97       | 81.44                         | 82.19\(^f\)      | 83.31       |
| \( \text{C}_6\text{H}_5\text{NO}_2 \) | 87.93       | 85.63                         | 87.42\(^f\)      | 90.09       |
| \( \text{C}_6\text{F}_6 \) | 72.79       | 71.45                         | —                | 71.40       |

\(^a\) Global hybrid density functional: B3LYP/aug-cc-pVTZ, Ref. 64.
\(^b\) Range-separated hybrid density functional: \( \omega \text{B97X-D}/\text{aug-cc-pVTZ}, \) Ref. 65.
\(^c\) Coupled-cluster method: CC3/aug-cc-pVTZ, Ref. 63.
\(^d\) Composite (hybrid) SDQ-MP4 value, Ref. 66.
\(^e\) 2nd order Møller-Plesset perturbation theory: MP2/\text{aug-cc-pVTZ}, Ref. 65.
\(^f\) This work.

### Table II. Molar refractivity \( R \) (in \( \text{cm}^3\text{mol}^{-1} \)) as a function of wave length \( \lambda \) (in nm) for benzene.

| \( \lambda \) (nm) | DOSD\(^a\) | Experiment\(^b\) |
|---------------------|-------------|------------------|
| 644.02              | 68.19       | 26.19            |
| 546.23              | 26.68       | 26.54            |
| 508.72              | 26.88       | 26.75            |
| 480.13              | 27.07       | 26.96            |
| 435.96              | 27.45       | 27.36            |

\(^a\) This work.
\(^b\) Ref. 40.

### Table III. Frequency-dependent polarizability \( \alpha(\omega) \) (in au) as a function of wave length \( \lambda \) (in nm).

| Molecule              | Method | \( \lambda = 632 \text{ nm} \) | \( \lambda = 488 \text{ nm} \) |
|-----------------------|--------|-----------------------------|-----------------------------|
| Benzene               | CC3\(^a\) | 70.86                       | 72.63                       |
|                      | DOSD\(^b\) | 70.51                       | 72.26                       |
| Pyridazine            | CC3\(^a\) | 60.62                       | 62.07                       |
|                      | DOSD\(^b\) | 58.76                       | 60.01                       |
| Pyrimidine            | CC3\(^a\) | 59.76                       | 61.11                       |
|                      | DOSD\(^b\) | 58.74                       | 60.04                       |
| Pyrazine              | CC3\(^a\) | 60.89                       | 62.50                       |
|                      | DOSD\(^b\) | 59.09                       | 60.64                       |
| s-Triazine            | CC3\(^a\) | 53.65                       | 54.77                       |
|                      | DOSD\(^b\) | 53.65                       | 54.77                       |
| Toluene               | DOSD\(^b\) | 86.16                       | 88.31                       |
| \( \text{C}_6\text{H}_5\text{NO}_2 \) | DOSD\(^b\) | 93.65                       | 96.46                       |
| \( \text{C}_6\text{F}_6 \) | DOSD\(^b\) | 73.32                       | 74.77                       |

\(^a\) Coupled-cluster method: CC3/\text{aug-cc-pVTZ}, Ref. 63.
\(^b\) This work.

### D. Sum rules and mean excitation energies

The dipole sum rules \( S(k) \) for \(-6 \leq k \leq 2\) are listed in Table IV. Many important physical proper-

\[ \text{...} \]
ties are related to the $S(k)$. The Taylor expansion of the frequency-dependent polarizability $\alpha(\omega)$ valid for frequencies $\omega$ below the lowest excitation frequency $\omega_1$ is

$$\alpha(\omega) = S(-2) + \omega^2 S(-4) + \omega^4 S(-6) + \cdots$$

(16)
in which $S(-2) = \alpha(0)$ is the static electronic dipole polarizability and the $S(-2k - 2)$ with $k = 1, 2, \ldots$ are called Cauchy moments. $S(2)$ is proportional to the sum of the electron density values at the nuclei, and $S(-1)$ is related to the total differential cross-section for inelastic scattering in collisions of charged-particles with the molecule.

As can be verified in Table IV the DOSDs are constrained to satisfy the KRT sum rule: $S(0) = N_e$, where $N_e$ is the number of electrons in the molecule. The benzene $S(k)$ reported by Kumar and Meath differ from those in Table IV by 4.6% and 4.3% for $k = 2$ and 1, respectively, and by $-1.8\%$, $-0.6\%$, $0.8\%$, $2.3\%$, $4.0\%$, and $5.9\%$ for $k = -1$ to $k = -6$, respectively.

The mean excitation energies $I(k)$ are listed in Table V. The average energy associated with the total inelastic scattering cross-section for grazing collisions of fast charged particles with the target species is $I(-1)$. The average energies $I(0)$ and $I(1)$ which are respectively related to the average energy loss (stopping power) and its mean fluctuation (straggling) in these collisions are required in radiation damage theory. $I(2)$ is related to the Lamb shift. The benzene $I(k)$ reported by Kumar and Meath differ from those in Table V by 4.7%, $-0.4\%$, $5.9\%$, $-0.8\%$ and $-1.2\%$ for $k = 2, 1, 0, -1$, and $-2$ respectively.

### E. Dispersion coefficients

The ten-term pseudospectra given in the supplementary material were used to calculate the spherically averaged $C_6$ dispersion coefficients listed in Table VI for interactions between pairs of the eight (hetero)aromatic molecules. The uncertainties in the $C_6$ coefficients are estimated to be in the $\pm4\%$ to $\pm8\%$ range depending upon the quality of the underlying DOSDs for the two species involved. The current value of 1765 au for benzene is 2.4% larger than and supersedes the older value of $C_6 = 1723$ au.

Induced-dipole-induced-dipole $C_6$ coefficients are essential ingredients in the construction of model, non-retarded, intermolecular potentials that are valid for all intermolecular distances. Moreover, they can assist in the calibration of calculated intermolecular potentials. If the first two dispersion coefficients $C_6$ and $C_8$ in the long-range interaction energy expansion $V(R) = -C_6/R^6 - C_8/R^8 - C_{10}/R^{10} - \cdots$ are available, then $C_{10}$ and higher-order coefficients can be calculated to good accuracy from simple models.

The supplementary material lists $C_6(A-B)$ coefficients for unlike ($A\neq B$) interactions in which $A$ is one of the eight aromatic molecules considered here and $B$ is one of 75 other species for which published pseudospectra are available. These 600 $C_6$ coefficients together with those in Table VI constitute a moderately large, self-consistent set of $C_6$ coefficients. This test set facilitates a timely, contemporary assessment of a well-regarded approximation:

$$C_6(A-B) = 2C_6(A-A)C_6(B-B)\alpha_A\alpha_B/C_6(A-A)\alpha_A^2 + C_6(B-B)\alpha_B^2,$$

(17)
in which $\alpha_A$ and $\alpha_B$ are the mean static polarizabilities of species $A$ and $B$, respectively. Equation (17) is sometimes called the Moelwyn-Hughes combination rule because it was published first in his textbook. However, it is quite
likely that Eq. (17) was known prior to that because it follows rather simply from the London approximation for \( C_6 \). All that is needed is to eliminate the Unsöld average energies from Eq. (13') in London’s later paper using his Eq. (13) from the same paper.

The mean absolute percent deviation of Eq. (17) from the DOSD values is only 0.23%. The predictions of Eq. (17) are in error by less than 1% in 606 (95.4%) of the 628 cases, and the error does not exceed 2.25% in the worst case. Interestingly, Eq. (17) is more likely to underestimate than overestimate the DOSD value; it predicts an underestimate in 400 of the 628 cases examined.

### IV. WHAT NEXT?

The DOSDs constructed in this work for seven aromatic molecules plus the improved DOSD for benzene increase significantly the number of molecules for which reliable and complete DOSDs have been determined primarily from experimental photoabsorption data. None of the new DOSDs incorporate a refractivity constraint unlike many, if not most, DOSDs built in the past using various versions of the method used here. This is encouraging because there are not too many more molecules for which gas-phase refractivity data is available.

However, an examination of the MPI-Mainz UV/VIS Spectral Atlas suggests that photoabsorption data from the absorption threshold to at least 30 eV, a range sufficient to construct a complete DOSD, is available for only about 20 more molecules. Once DOSDs for them are constructed, as they surely will be in the near future, what is the avenue for further progress? Obviously, experimental measurement of photoabsorption cross-sections for more species is one.

A different path is to find robust, black-box-like, additive models that are sufficiently accurate in the 10 eV to 30 eV range. That would open up the possibility of constructing complete DOSDs for the hundreds of molecules for which photoabsorption cross-sections are available in a restricted energy range from the absorption threshold up to about 10 eV. Free-atom and fragment additive models are at levels 1 and 4 in the additive model hierarchy. Level 2 additive models using dressed atoms and level 3 models based on atoms that depend upon their environment deserve a closer look for photoabsorption cross-sections. Preliminary work along these lines is under way.

### SUPPLEMENTARY MATERIAL

See the supplementary material for tables of \( C_6 (A-B) \) coefficients for unlike \( (A \neq B) \) interactions in which \( A \) is one of the eight aromatic molecules treated in this work and \( B \) is one of 75 other species, ten-term pseudospectra for the eight aromatic molecules, and references to the published pseudospectra for the 75 other species.

### DATA AVAILABILITY

The data that supports the findings of this study are available within the article and its supplementary material.

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### TABLE VI. Dispersion coefficients \( C_6(A-B) \) (in au). Multiplication of an entry by 6934 yields a value in K Å\(^6\).

| A—B                  | \( C_6 \) | A—B                  | \( C_6 \) |
|----------------------|----------|----------------------|----------|
| Benzene—Benzene      | 1765     | Pyrimidine—Toluene   | 1857     |
| Benzene—Pyridazine   | 1531     | Pyrimidine—C\(_6\)H\(_5\)NO\(_2\) | 2009     |
| Benzene—Pyrimidine   | 1523     | Pyrimidine—C\(_6\)F\(_6\) | 1775     |
| Benzene—Pyrazine     | 1507     | Pyrazine—Pyrazine    | 1288     |
| Benzene—s-Triazine   | 1419     | Pyrazine—s-Triazine  | 1213     |
| Benzene—Toluene      | 2153     | Pyrazine—Toluene     | 1838     |
| Benzene—C\(_6\)H\(_5\)NO\(_2\) | 2328     | Pyrazine—C\(_6\)H\(_5\)NO\(_2\) | 1988     |
| Benzene—C\(_6\)F\(_6\) | 2050     | Pyrazine—C\(_6\)F\(_6\) | 1756     |
| Pyridazine—Pyridazine| 1330     | s-Triazine—s-Triazine| 1143     |
| Pyridazine—Pyrimidine| 1332     | s-Triazine—Toluene   | 1730     |
| Pyridazine—Pyrazine  | 1308     | s-Triazine—C\(_6\)H\(_5\)NO\(_2\) | 1872     |
| Pyridazine—s-Triazine| 1233     | s-Triazine—C\(_6\)F\(_6\) | 1657     |
| Pyridazine—Toluene   | 1867     | Toluene—Toluene      | 2625     |
| Pyridazine—C\(_6\)H\(_5\)NO\(_2\) | 2020     | Toluene—C\(_6\)H\(_5\)NO\(_2\) | 2838     |
| Pyridazine—C\(_6\)F\(_6\) | 1785     | Toluene—C\(_6\)F\(_6\) | 2498     |
| Pyrimidine—Pyridazine| 1315     | C\(_6\)H\(_5\)NO\(_2\)—C\(_6\)H\(_5\)NO\(_2\) | 3070     |
| Pyrimidine—Pyrazine  | 1301     | C\(_6\)H\(_5\)NO\(_2—C\(_6\)F\(_6\) | 2707     |
| Pyrimidine—s-Triazine| 1226     | C\(_6\)F\(_6—C\(_6\)F\(_6\) | 2416     |
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