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van der Waals interactions of carbon monoxide*

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Padé approximant methods and experimental frequency dependent polarizabilities are used to calculate reliable van der Waals C_6 coefficients for the interaction of CO with He, Ne, Ar, Kr, Xe, H, Li, Na, K, Rb, Cs, H₂, N₂, O₂, CO₂, and CO. Error bounds are given for the C_6 coefficients and for the CO oscillator strength sums.

I. INTRODUCTION AND THEORY

In a recent paper¹ (hereinafter called I), one of us calculated van der Waals coefficients for CO₂ interactions using the Padé approximant methods of Langhoff and Karplus² to get the contribution to the polarizability from the ultraviolet part of its spectrum and the method of Nir, Adams, and Rein,³ which views molecular bands as lines of finite width, to get the infrared contribution. In this paper we use this method to calculate the first reliable van der Waals C_6 coefficients for interactions involving carbon monoxide, CO.

As is well known,⁴ the van der Waals C_6 coefficient for the interaction of a Σ -state diatomic molecule such as CO with an S-state atom takes the form

$$C_6 = C_6(0) + C_6(2) P_2(\cos \theta), \quad (1)$$

where θ is the angle between the molecular axis and the vector from the center of mass of the molecule to the atom, and P_2 is a Legendre polynomial. Here each coefficient includes both induction and dispersion contributions:

$$C_6(L) = C_6^{\text{ind}}(L) + C_6^{\text{dis}}(L). \quad (2)$$

The induction terms are simply given (in atomic units) by⁴

$$C_6^{\text{ind}}(0) = C_6^{\text{ind}}(2) = \alpha(A)\mu^2, \quad (3)$$

where μ is the permanent dipole moment of the molecule and $\alpha(A)$ is the static dipole polarizability of the atom. Using the experimental value⁵ $\mu(\text{CO}) = -0.112 \text{ D} = -0.0441 \text{ a.u.}$ consistent with the use of experimental polarizabilities, so that the resulting van der Waals potential has been averaged over the ground state vibrational motion, one obtains the $C_6^{\text{ind}}(L)$ directly.

If the polarizability anisotropy ratio, $\kappa = (\alpha_{\parallel} - \alpha_{\perp}) / (\alpha_{\parallel} + 2\alpha_{\perp})$, is known as a function of frequency, $C_6^{\text{dis}}(2)$ can be calculated accurately.⁶ Unfortunately, for CO values of κ have been reported at only two frequencies ($\kappa = 0.089_7$ at⁷ $\omega = 0.0720 \text{ a.u.}$ and 0.100 at⁸ 0.0934 a.u.), and their difference is opposite that necessitated by the spectrum of CO and thus wrong. We assume that the average of the two is the correct value and negligibly different from that at zero frequency. Then, as we have shown elsewhere,⁴ one can obtain reasonable bounds on $C_6^{\text{dis}}(2)$ from

$$C_6^{\text{dis}}(2) = a_6 C_6^{\text{dis}}(0), \quad (4)$$

with

$$\frac{\alpha_{\parallel}^{3/4} - \alpha_{\perp}^{3/4}}{\alpha_{\parallel}^{3/4} + 2\alpha_{\perp}^{3/4}} \leq a_6 \leq \kappa, \quad (5)$$

which gives the estimate

$$a_6 = 0.083 \pm 0.017 \quad (6)$$

for CO interactions.

The remaining part of C_6 , $C_6^{\text{dis}}(0)$, is determined in the following section using, with minor modifications, the method of Paper I, which briefly stated is as follows: The experimental frequency dependent polarizability is obtained from refractive index data using the Lorentz-Lorentz equation; then, it is fit using a finite linewidth dispersion term for the ir part and a Cauchy expansion for the uv part. Then, the resulting sum rules (coefficients of the Cauchy expansion) are used to construct upper and lower Padé bounds to the polarizability. From these, effective oscillator strengths and excitation frequencies are obtained from which upper and lower bounds to $C_6^{\text{dis}}(0)$ are obtained.

II. CALCULATIONS AND RESULTS

As input data we used values of the refractive index η of CO at 94 wavelengths ranging from 237, 9–13 000 nm reported by Ländolt and Bornstein⁹ and the International Critical Tables.¹⁰ We were unable to find any newer measurements. The frequency-dependent average polarizability [$\alpha = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$] was obtained at each frequency from the Lorentz-Lorentz equation³

$$\alpha(\omega) = \frac{3}{4\pi n} \left(\frac{\eta^2 - 1}{\eta^2 + 2} \right), \quad (7)$$

where n is the number density of CO molecules. The Benedict-Webb-Rubin equation of state for CO of

TABLE I. Oscillator strength sums for CO. The ultraviolet contributions were obtained directly from fitting Eq. (5) and the infrared contributions from expansion of the first term in Eq. (9) after fitting: $S(0)$ is from the Reiche-Thomas-Kuhn sum rule. All are in Hartree atomic units.

k	$S^{\text{uv}}(k)$	$S^{\text{ir}}(k)$	$S^{\text{tot}}(k)$
0	14.0000	1.37×10^{-5}	14.0000
-2	13.0891 ± 0.0002	0.142 ± 0.003	13.231 ± 0.003
-4	47.842 ± 0.055	1.48×10^3	1.53×10^3
-6	318.6 ± 5.7	1.51×10^7	1.51×10^7
-8	2800 ± 230	1.53×10^{11}	1.53×10^{11}
-10	26500 ± 3000	1.59×10^{15}	1.59×10^{15}

TABLE II. Effective oscillator strengths f_n , frequencies ω_n , and widths γ_n for CO. Here $A_n = f_n/\omega_n^2$. The parameters for $n=1$ were obtained from Eq. (9). On the others u and l label parameters from the upper and lower bounding Padé approximants. Hartree atomic units.

n	f_n	A_n	ω_n	γ_n
1	1.36874 E-5	0.1415644	9.832942 E-3	3.040752 E-4
2u	13.13886	6.919783	1.377947	0.0
2l	5.539610	9.959741	0.7457883	0.0
3u	0.8611361	6.169317	0.3736090	0.0
3l	0.3271316	3.129359	0.3233207	0.0

Schiller and Canjar¹¹ gives as the conversion factor from measurements at STP to $\alpha(\omega)$ in atomic units

$$3/(4\pi n) = 59926.98 a_0^3. \quad (8)$$

$\alpha(0)$ can also be obtained from dielectric constant measurements¹² via the Clausius–Mosotti equation,¹³ and the value $\alpha(0) = 13.21 \pm 0.13 a_0^3$ thus obtained is consistent with the $\alpha(0) = S(-2)$ determined below from refractive index data but sufficiently uncertain that it could not be used to improve accuracy.

The experimental $\alpha(\omega)$ were then fit by the formula (see Paper I)

$$\text{Re}\alpha(\omega) = \frac{A_1[1 - (\omega/\omega_1)^2]}{[1 - (\omega/\omega_1)^2]^2 + (\gamma_1\omega/\omega_1^2)^2} + \sum_{k=0}^4 S^{uv}(-2k-2)\omega^{2k}, \quad (9)$$

where the first term is the contribution of the ir spectrum of CO, and the uv contribution has been expanded in a Cauchy series. The parameters in (9) were determined by an iterative procedure in which the three parameters in the ir term and $S(-10)$ were calculated using a nonlinear flexible tolerance minimization program¹⁴ which included the Stieltjes constraints,² and $S(-2)$ through $S(-8)$ were calculated using a linear least squares method. This procedure gave a root mean square deviation of $0.041 a_0^3$, which is half that of the 2 term fit of Nir, Adams, and Rein.³

The resulting oscillator strength sums $S^{uv}(k)$ are given in Table I. These were used to calculate the [2, 1] Padé approximants² from which the effective oscillator strengths and effective frequencies of Table II and upper and lower bounds to the $C_6^{\text{dis}}(0)$ could be obtained as in Paper I. However, the Padé methods treat the $S^{uv}(k)$ as though they were exact and had been determined with an infinite number of terms in the summation in Eq. (9). To get an estimate of the additional error thus introduced, we varied $S^{uv}(-10)$, which is not needed by the [2, 1] Padé approximants, over the entire range allowed by the Stieltjes constraints to see what values of the other $S(k)$ and of $C_6^{\text{dis}}(0)$ that would generate. That gave the error limits shown in Table I, but because the original data were quite smooth and the uncertainties in the $S(k)$ are quite small, it only widened the error bounds on the $C_6^{\text{dis}}(0)$ slightly.

The resulting $C_6^{\text{dis}}(0)$ for the interaction of CO with a number of partners (using the sum rules from Refs. 1 and 2 for the other atoms and molecules) are given in Table III. The numbers shown are the means of the best Padé bounds, but the uncertainties include the range of values generated by the uncertainties in the $S(k)$. Also in Table II are the induction and angle-dependent parts of C_6 for the partners for which Eq. (1)–(3) are adequate. The induction terms are very small because the dipole moment of CO is so small.

Before concluding we note that the C_6 coefficients discussed herein are only defined within the Born–Oppenheimer approximation, and only the *electronic* polarizability should be used in calculating $C_6^{\text{dis}}(0)$. In a future publication,⁴ we discuss the vibrational coordinate dependence of C_6 in detail and show that, to a good approximation, the experimental quantities needed in calculating C_6 are the $S^{uv}(k)$ rather than the $S^{\text{tot}}(k)$. In the present case the ir spectrum of CO contributes only about 1% of the static polarizability, and inclusion of the ir contribution ($n=1$ term of Table II) would change the C_6^{dis} of Table III by a completely negligible amount (less than 0.1%). In our previous paper on CO₂ C_6 coef-

TABLE III. Van der Waals C_6 coefficients for the interaction of CO with various partners. All are in Hartree atomic units ($e^2 a_0^5$).

Partner	$C_6^{\text{dis}}(0)$	$C_6^{\text{ind}}(0)$	$C_6^{\text{tot}}(0)$	$C_6^{\text{dis}}(2)$	$C_6^{\text{ind}}(2)$	$C_6^{\text{tot}}(2)$
H	23.0 ± 0.9	8.74 E-3	23.0 ± 0.9	1.92 ± 0.47	8.74 E-3	1.92 ± 0.47
Li	201.9 ± 4.1	3.18 E-1	202.2 ± 4.1	16.8 ± 3.8	3.18 E-1	17.1 ± 3.8
Na	246 ± 16	3.25 E-1	247 ± 16	20.5 ± 5.7	3.25 E-1	20.8 ± 5.7
K	363 ± 24	5.59 E-1	364 ± 24	30.3 ± 8.4	5.59 E-1	30.8 ± 8.5
Rb	412 ± 28	6.13 E-1	412 ± 28	34.3 ± 9.7	6.13 E-1	34.9 ± 9.7
Cs	355 ± 16	6.92 E-1	356 ± 16	29.6 ± 7.5	6.92 E-1	30.3 ± 7.6
He	11.2 ± 0.8	2.69 E-3	11.2 ± 0.8	0.93 ± 0.27	2.69 E-3	0.93 ± 0.27
Ne	23.8 ± 2.5	5.18 E-3	23.8 ± 2.5	1.98 ± 0.65	5.18 E-3	1.98 ± 0.65
Ar	78.2 ± 7.6	2.15 E-2	78.2 ± 7.6	6.5 ± 2.1	2.15 E-2	6.5 ± 2.1
Kr	111 ± 12	3.25 E-2	111 ± 12	9.3 ± 3.0	3.25 E-2	9.3 ± 3.1
Xe	192 ± 25	5.31 E-2	192 ± 25	16.0 ± 5.7	5.31 E-2	16.0 ± 5.7
H ₂	32.1 ± 1.5					
N ₂	80.7 ± 6.9					
O ₂	62.8 ± 3.3					
CO ₂	128.6 ± 8.7					
CO	88.4 ± 9.7					

ficients,¹ this ir contribution was inadvertently included, and the C_6 coefficients obtained there should be revised downward by about 1% (which is still well within the stated uncertainty).

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