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Interaction second virial coefficients from a recent H₂-CO potential energy surface

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I. INTRODUCTION

Astronomers use spectra of carbon monoxide to determine temperatures and particle densities in molecular clouds. Collisions with the predominant H₂ molecules in the clouds affect the populations of CO internal states. Numerical cloud models, therefore, need quantitative estimates of state to state cross sections and rate coefficients for H₂-CO collisions (for two examples, see Refs. 1 and 2). These quantities are difficult to measure, and must be calculated from accurate H₂-CO potential surfaces. Occasionally a paper appears in the astrophysics literature giving the best current estimates of the cross sections and rate coefficients.³⁻⁵ The most recent is that of Schinke *et al.* from 1985.⁵ They used a "Hartree-Fock plus dispersion" potential whose repulsive part was determined by self-consistent field calculations and whose dispersion damping coefficients were adjusted to match crossed molecular beam scattering data.

In 1998 Jankowski and Szalewicz published a new *ab initio* H₂-CO potential⁶ determined by symmetry adapted perturbation theory (SAPT).⁷ This new potential gives reasonable agreement with infrared (IR) absorption data on *p*H₂-CO van der Waals clusters.⁸ It appears to be a good candidate for new calculations of state to state H₂-CO cross sections for use in astronomy.

At least three comparisons between predictions of the SAPT surface and experimental data are under way: further work on the van der Waals spectra and extension to *o*H₂-CO,⁹ comparisons with extensive measurements of CO pressure broadening by H₂,¹⁰ and comparisons with state to state inelastic cross sections and thermally averaged depopulation cross sections.¹¹ We thought it worthwhile to check the new surface against existing measurements of interaction second virial coefficients for H₂-CO mixtures as well. These coefficients are sensitive to the volume and depth of the potential well at low temperatures and to the volume of the repulsive core at high temperatures. They give a global measure of the quality of a potential model and can be measured accurately. Several sets of virial coefficient measurements for H₂-CO are available.^{12,13} The more recent ones are a very low temperature set (36-60 K) calculated by Reuss and Beenakker¹⁴ from the solid-vapor equilibrium data of Dokoupil *et al.*,¹⁵ and a set between 77 and 296 K determined by Schramm *et al.*¹³ In this Note we describe the computation of these coefficients from the SAPT potential and compare them to the experimental data.

II. CALCULATIONS

We evaluated interaction second virial coefficients from the SAPT potential using formulas given by Pack¹⁶ and Hirschfelder, Curtiss, and Bird (HCB).¹⁷ The classical coefficient $B^{(0)}$ was determined with Eq. (6.7-2) of HCB. The first quantum corrections $B_r^{(1)}$ and $B_a^{(1)}$ were calculated with Eqs. (21) and (20) of Pack; radial expansion coefficients were constructed by quadrature. The second radial quantum corrections $B_r^{(2)}$ (proportional to \hbar^4) were calculated by extending Eq. (6.5-6) of HCB to the full four-dimensional integration.

Angular integrations were performed with Gauss-Legendre quadrature in $\cos \theta_1$, $\cos \theta_2$, and ϕ . The radial integral was divided into two parts: one from 0 to a small radius r_0 within which the term $\exp(-V(r, \theta_1, \theta_2, \phi)/kT)$ was set to zero, and one from r_0 to infinity which was evaluated by Gauss-Legendre quadrature in $1/r$. The computed values were independent of the value of r_0 over a reasonable range within the hard core of the potential. The reduced mass of the H₂-CO system was taken as 1.88027 amu, and the H₂ and CO rotational constants were 59.322 and 1.9225165 cm⁻¹, respectively.

III. RESULTS

The contributions to the computed virial coefficients are listed in Table I. The angular first order quantum correction is broken into the "orbital" or Coriolis term $B_{a\mu}^{(1)}$ and the "rotational" terms $B_{al}^{(1)}$. The numerical quadrature is converged to ± 0.001 cm³/mol; remaining errors arise from truncation of the Wigner-Kirkwood expansion in \hbar^2/m , neglect of vibrational motions of CO and H₂, and errors in the potential.

At 77 K the radial second-order correction is about 10% of the corresponding first-order one, or about 1% of the total. The relative magnitudes of the angular and radial first-order corrections suggest that the second- and higher-order angular and mixed radial/angular terms probably do not contribute more than 2 cm³/mol. Below 77 K, the first- and second-order quantum corrections rapidly become more important; we have not compared with the very low temperature data because the first-order angular expansion is probably insufficient there.

IV. DISCUSSION

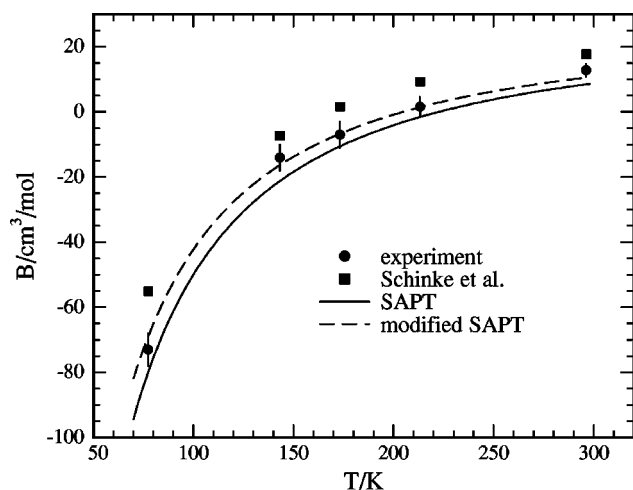
Figure 1 shows the experimental data of Schramm *et al.*,¹³ the values we computed from the SAPT potential,

TABLE I. Contributions to calculated interaction second virial coefficients for H₂-CO, from the *ab initio* SAPT surface. The experimental values are from Ref. 13. All terms have units of cm³/mol.

<i>T</i> /K	<i>B</i> ⁽⁰⁾	<i>B</i> _{<i>r</i>} ⁽¹⁾	<i>B</i> _{<i>r</i>} ⁽²⁾	<i>B</i> _{<i>aμ</i>} ⁽¹⁾	<i>B</i> _{<i>al</i>} ⁽¹⁾ (H ₂)	<i>B</i> _{<i>al</i>} ⁽¹⁾ (CO)	<i>B</i> _{tot}	<i>B</i> _{exp}
77.30	-97.218	10.644	-1.195	0.416	6.614	0.669	-80.071	-73±5
143.15	-24.861	2.690	-0.112	0.080	0.849	0.140	-21.214	-14±4
173.15	-13.002	1.874	-0.058	0.053	0.479	0.093	-10.561	-7±4
213.15	-3.179	1.293	-0.029	0.035	0.263	0.062	-1.556	1.6±3
296.15	7.605	0.747	-0.010	0.019	0.108	0.034	8.502	12.8

and the values computed by Buck from the potential of Schinke *et al.*¹³ The coefficients computed from the Schinke potential are consistently above the experimental data. Those computed from the SAPT potential are consistently below, though the discrepancies are generally smaller. The comparison with experiment indicates that the potential well of the SAPT surface is too deep or has too large a volume. Since the IR data indicate that the shape of the SAPT well is reasonable,^{6,8} the error is probably in the depth.

To estimate the size of the error, we performed additional calculations with a modified SAPT potential. Potential energies in the van der Waals well were multiplied by a factor *f* that was adjusted to obtain the best fit to the experimental data. Schramm *et al.* list two experimental values of *B* at 296.15 K: a literature value of 13.5 cm³/mol, and their own value of 12.8 cm³/mol. The optimum value of *f* was sensitive to which of the values we used. We chose the lower value because it appears more consistent with the data at lower temperatures. We assigned it an uncertainty of 2 cm³/mol for purposes of χ^2 fitting. The resulting optimum value of *f* was 0.93, with a 68% confidence interval ($\Delta\chi^2 = 1$) of [0.91, 0.96]. The resulting virial coefficients are shown in Fig. 1 as a dashed line. A nearly identical result was obtained if the entire potential surface, and not just its attractive part, was scaled by *f*. Had we chosen the larger experimental value for the 296.15 K virial coefficient, the optimum *f* would be about 0.91 and the agreement with the 77 K measurement would be poorer.

FIG. 1. Interaction second virial coefficients for H₂-CO.

The scaled surface should not be expected to show better agreement with any experiments other than second virial coefficient measurements. We have used the scaling merely to provide a quantitative estimate of the error in the well depth of the SAPT potential.

V. CONCLUSION

The SAPT surface of Jankowski and Szalewicz represents an improvement over earlier surfaces but does not achieve complete agreement with the experimental virial coefficient data. The van der Waals well of the SAPT potential appears to be too deep by 4%–9%.

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