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ON THE USE OF PRESSURE BROADENING DATA TO ASSESS THE ACCURACY
OF CO-He INTERACTION POTENTIALS.

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Rate constants for rotational excitation of CO by collisions with low energy He atoms are of some importance for interpreting radioastronomical data. Since experimental values are not available extensive theoretical calculations for this system have been presented by Green and Thaddeus¹ and Green and Chapman.² The major source of error in those studies undoubtedly came from inaccuracies in the intermolecular potential which was obtained from the Gordon-Kim³ electron gas model, modified somewhat at intermediate and large separations to conform with the correct asymptotic multipole limit and with information available from beam scattering experiments. In Ref. 1, the adequacy of the electron gas surface was tested by comparing with experimental pressure broadening data since these sample the same parts of the potential as inelastic state-to-state cross sections; agreement with experiment was found to be acceptable, i.e., within the 10% experimental uncertainty. (See also Ref. 4.)

Comparisons of the electron gas model with more rigorous ab initio potentials have been reported for a few other systems;⁵ these suggest that the model may not be quantitatively accurate although it gives a fairly good description of the short-range anisotropies. Recently, Kraemer and Dierksen^{6a} have obtained the CO-He potential from extensive self-consistent field and configuration interaction (SCF-CI) calculations and compared it with the electron gas surface reported in Ref. 1. In addition, Thomas et al.,^{6b} have computed state-to-state integral cross sections from this potential and compared them with values from the electron gas potential. These comparisons revealed qualitative differences in the energy dependence of the elastic cross sections and quantitative differences (in the range 30-200%) in inelastic cross sections.

The purpose of the present Note is to consider the agreement of the more accurate, SCF-CI surface with pressure broadening data. Since pressure broadening traditionally has been used to obtain information about intermolecular forces, it is of particular interest to inquire whether these two surfaces predict any differences in pressure broadening which might provide a means of differentiating among them on the basis of experimental data.

In order to provide the most direct comparison, new scattering calculations have been performed for both the electron gas and SCF-CI potentials. In particular, coupled states calculations which included CO rotational levels through $J=7$ (CS/B7) were performed at collision energies of 15 and 30 cm^{-1} . Somewhat larger, CS/B9 calculations were done for collision energies of 60, 110, 200, and 400 cm^{-1} . The coupled states scattering approximation has been shown to agree to within a few percent with essentially exact close coupling values for this system, with accuracy improving at higher energies.⁷ Calculations at collision energies of 800 and 1200 cm^{-1} were done within the infinite order sudden approximation, with the orientation dependence treated by a 28-point Gauss integration.⁸ Similar calculations at 400 cm^{-1} agreed with the CS/B9 results to 3% and accuracy should improve at higher energies. Results are presented in Table I.

Boltzmann averages over collision energy have been performed to compare with experimental results at liquid nitrogen (77 K), dry ice (195 K), and room (295 K) temperatures. Theoretical values are compared with the available microwave experimental data⁹ in Table II. The various scattering approximations and numerical methods used here are thought to provide values within 5% of exact values for each

potential with the possible exception of the lowest energies and temperature where effects of resonances may not have been fully included. Since identical calculations were done for both potentials, differences between the cross sections from the two surfaces should be predicted more accurately than this. (Small discrepancies -- less than a few percent -- between electron gas values reported here and those in Ref. 1 can be traced to use of the coupled states approximation versus full close coupling and to the use of different collision energies and numerical integration method to obtain the Boltzmann average.)

Consideration of the comparisons of theory and experiment in Table II leads to the following conclusions. The cross sections from the SCF-CI potential would appear to be in marginally better agreement with experiment than those from the electron gas potential. This conforms to the expectation that the former is more accurate than the latter. Within the quoted experimental uncertainties, however, either potential could be judged to be consistent with the data. In this sense, pressure broadening data is not a very severe constraint on details of the potential. On closer examination it appears that this is due not so much to the inherent insensitivity of pressure broadening data to details of the potential as to the sizeable uncertainties in the experimental values. While both potentials predict essentially the same value for room temperature broadening of the 0-1 transition, there are significant differences in the predicted dependence on temperature and on spectroscopic level. The electron gas potential predicts an increase in pressure broadening cross sections with decreasing temperature whereas the SCF-CI potential predicts a very small decrease in cross sections with decreasing temperature.

Also, the electron gas potential predicts a more rapid decrease of cross section for higher spectral transitions than does the SCF-CI potential. Unfortunately, both of these effects amount to changes of a few percent. Thus, significantly more accurate experimental values would be required than are currently available in order to place meaningful constraints on the intermolecular potential.

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Cross sections in \AA^2 for pressure broadening of CO by He from scattering calculations using (1) an electron gas intermolecular potential, upper values, and (2) an SCF-CI potential, lower values.

<u>Energy, cm^{-1}</u>	<u>Spectral line, j-j'</u>			
	<u>0-1</u>	<u>1-2</u>	<u>2-3</u>	<u>3-4</u>
15	63.35 26.34	48.61 25.38	31.26 32.69	32.19 33.43
30	46.96 27.37	38.34 26.08	34.04 25.31	30.66 26.79
60	35.63 27.16	31.76 25.81	29.84 25.70	28.26 25.73
110	30.24 26.56	27.60 25.36	26.58 25.16	26.00 25.25
200	27.33 26.91	25.32 25.56	24.61 25.21	24.17 25.15
400	25.61 28.17	24.04 26.77	23.40 26.32	23.06 26.13
800	24.68 28.94	23.65 27.95	23.17 27.54	22.90 27.35
1200	24.16 28.59	23.26 27.72	22.86 27.35	22.62 27.14

Comparison of theoretical and experimental Co-He effective pressure broadening cross sections (\AA^2).

<u>Spectral line</u>	<u>Temperature, K</u>	<u>EG</u> ^a	<u>SCF-CI</u> ^b	<u>expt.</u> ^c
0-1	77	34.8	26.6	28±3
	195	28.9	27.3	27±3
	295	27.3	27.7	27±3
1-2	77	30.5	25.4	...
	195	26.4	26.0	...
	295	25.3	26.5	29±6
2-3	77	27.9	25.5	...
	195	25.3	25.8	...
	295	24.5	26.1	...

a. Electron gas intermolecular potential from Ref. 1.

b. SCF-CI potential from Ref. 6.

c. Nerf and Sonnenberg, Ref. 9, and Nerf, private communication.

