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LOW ANGLE SCATTERING OF  $\text{Li}^+$  by CO

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LOW ANGLE SCATTERING OF  $\text{Li}^+$  by CO

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Abstract

Classical trajectory calculations have been done for the distribution of final rotational angular momentum of CO after the scattering of  $\text{Li}^+$  ions at center-of-mass angle  $10^\circ$  and relative kinetic energy 4.28 eV. The width of the distribution and the location of the classical rotational rainbows are in good agreement with the experimental results. CI calculations are reported for new points on the potential energy surface which demonstrate that the surface used in previous studies was not converged in the Legendre polynomial expansion of its angular dependence.

It has been previously suggested<sup>1</sup> that rainbow structure found in the classical distribution of final rotational angular momentum of CO after collisions with  $\text{Li}^+$  ions, is a possible explanation for apparently similar structure in the experimental time-of-flight spectra<sup>2</sup> for this system. Recent low-angle scattering experiments<sup>3</sup> confirm the existence of structure in the time-of-flight spectrum and we report here on the corresponding classical trajectory calculations.

Structure of this type has also been recently reported for K- $\text{N}_2$  and K-CO scattering by Schepper, Ross and Beck.<sup>4,5</sup> Their analysis of classical scattering from a rigid, hard-shell ellipsoid<sup>4-6</sup> also leads to a rotational rainbow explanation of the structure and gives a good qualitative description of their experiments. Bergmann *et al.*<sup>7</sup> also report rotational rainbow structure in their He- $\text{Na}_2$  experiments. Additional theoretical work in this area has also recently appeared.<sup>8,9,10</sup>

The quantity of interest is the differential cross section at fixed scattering angle and energy as a function of the final rotational angular momentum quantum number,  $j$ , of CO. At 4.23 eV and angles  $30^\circ$ - $50^\circ$ , the classical trajectory results<sup>1</sup> are not in good agreement with the experiment.<sup>2</sup> The calculated distribution is considerably contracted compared to experiment. It has been demonstrated that inclusion of the vibrational degree of freedom has little effect on this.<sup>11</sup> On the other hand, because of the high energy and large number of energetically accessible states, classical mechanics should give a reasonably good description of the dynamics. Comparisons with coupled states calculations at 1 eV also indicate

this to be so.<sup>12</sup> Assuming the experiments to be correct, which we do, this leaves the potential energy surface suspect. It is unlikely, however, that more elaborate CI calculations and usage of more extended basis sets to describe the molecular orbitals more accurately would produce much change in the points which have already been computed. Therefore, the reason for the discrepancy is suspected to be that due to the anisotropy of the potential, particularly in the repulsive region, simply not enough points have been computed on the potential energy surface.

The angular dependence of the potential energy surface was expanded in Legendre polynomials of  $\cos(\theta)$ , where  $\theta$  is the angle between the CO axis and the vector from the CO center of mass to the  $\text{Li}^+$  ion. A 5 term expansion was used. For the high scattering angle study, the classical trajectories all had turning points in the region of  $R = 3.0$  au, where  $R$  is the distance from  $\text{Li}^+$  and the CO center of mass. We have computed eight additional points at  $R = 3.0$ , given in table 1. Expansions in 7, 9, 11 and 13 Legendre polynomials were done using the 5 angles from ref. 4 and including the additional points in the order they appear in table 1. The results in figure 1 show that indeed at least 9 angles are necessary for convergence. At  $\theta = 90^\circ$  the 5 angle expansion even has the wrong sign for the slope meaning that the force there is in the wrong direction.

For scattering at  $30^\circ$ - $50^\circ$  the turning points of the trajectories are well up on the repulsive wall region of the potential where the anisotropy, as we have just indicated, is strong. However, for

scattering at  $10^\circ$  the turning points are around  $R = 5.0$  which is in the potential well region where the anisotropy is weaker. The  $5^\circ$  angle expansion should be more nearly converged here than at  $R = 3.0$  and consequently we might expect the classical cross sections to be in better agreement with the experiment.

Figure 2 shows the results of an 11200 trajectory study at 4.28 eV relative kinetic energy with CO initially in the  $j = 1$  state. Trajectories were counted in a  $6^\circ$  interval centered at a scattering angle of  $10^\circ$ , and an interval of  $\Delta j = 1$  centered on integer  $j$ -values. The boxes indicate the standard deviation or 68 percent confidence interval from the Monte Carlo sampling. Also shown in figure 2, scaled to the maximum in the computed values, are the center-of-mass cross sections inferred from the experiment<sup>3</sup>. The comparison is encouraging. The classical distribution in final  $j$  is not contracted compared to the experimental one as was true at higher scattering angles. Even more interesting, however, is the good agreement in the location of the structure. Between  $j = 6$  and 16 there are 3 or 4 closely spaced rainbow peaks in the classical results corresponding well to the experimental peak at  $j = 13$ . The classical rainbow peaks at  $j = 19$  and  $j = 25$  are also in excellent agreement with the experimental peaks at  $j = 20$  and  $j = 26$ .

The present results support the rotational rainbow explanation of the structure in the experimental spectrum. They also support the contention that the chief reason for disagreement between previous classical calculations and experiment is an insufficient number of

potential energy surface points. We hope to compute the needed extra points and repeat the higher scattering angle, classical trajectory calculations in the future.

### Acknowledgment

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## References

- [ 1] L. D. Thomas, J. Chem. Phys. 67 (1977) 5224
- [ 2] R. Bottner, U. Ross and J. P. Toennies, J. Chem. Phys. 65 (1976)  
773
- [ 3] W. Eastes, U. Ross and J. P. Toennies, Chem. Phys. 39 (1979) 407
- [ 4] W. Schepper, U. Ross and D. Beck, Z. Physik A 290 (1979) 131
- [ 5] D. Beck, U. Ross and W. Schepper, Phys. Rev. A 19 (1979) 2173
- [ 6] D. Beck, U. Ross and W. Schepper, preprint
- [ 7] K. Bergmann, R. Engelhardt, U. Hefter and J. Witt, J. Chem.  
Phys. 71 (1979) 2726
- [ 8] R. Schinke, Chem. Phys. 34 (1978) 65
- [ 9] J. M. Bowman, Chem. Phys. Lett. 62 (1979) 309
- [10] R. Schinke and P. McGuire, J. Chem. Phys. 71 (1979) 4201
- [11] L. D. Thomas, W. P. Kraemer and G. H. F. Diercksen, Chem. Phys.  
30 (1978) 33
- [12] L. D. Thomas, W. P. Kraemer, G. H. F. Diercksen and P. McGuire,  
Chem. Phys. 27 (1978) 237

Table 1. Interaction energy  $V(R,\theta)$   
at  $R = 3.0$  au for  $\text{Li}^+ - \text{CO}$   
in units of 27.21 eV.

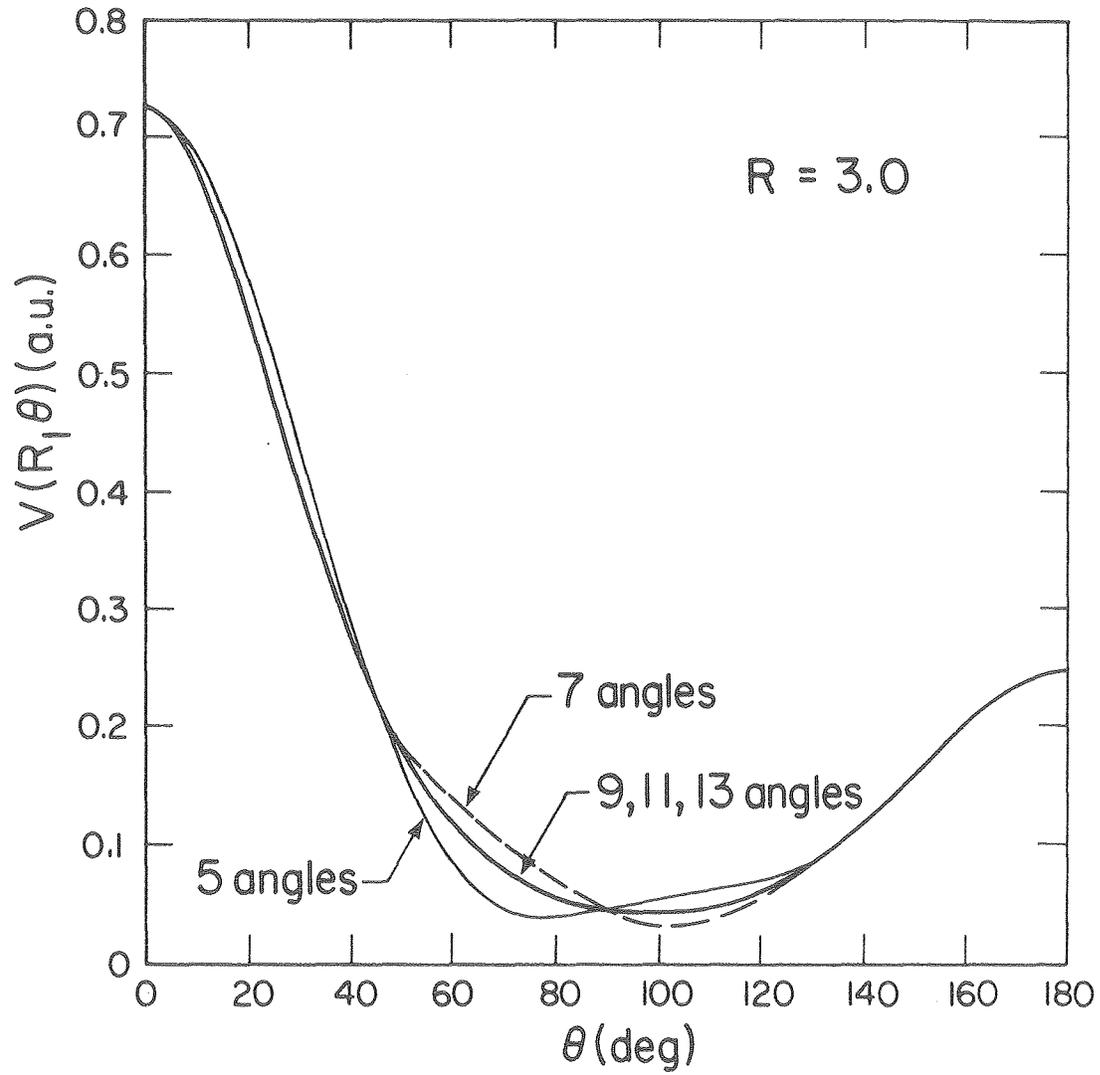
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$\theta$	$V(R,\theta)$
31.8	0.37794666
148.2	0.15022034
81.4	0.05448210
98.6	0.04222616
72.5	0.07230830
107.5	0.04501255
60.0	0.11858767
120.0	0.06009969

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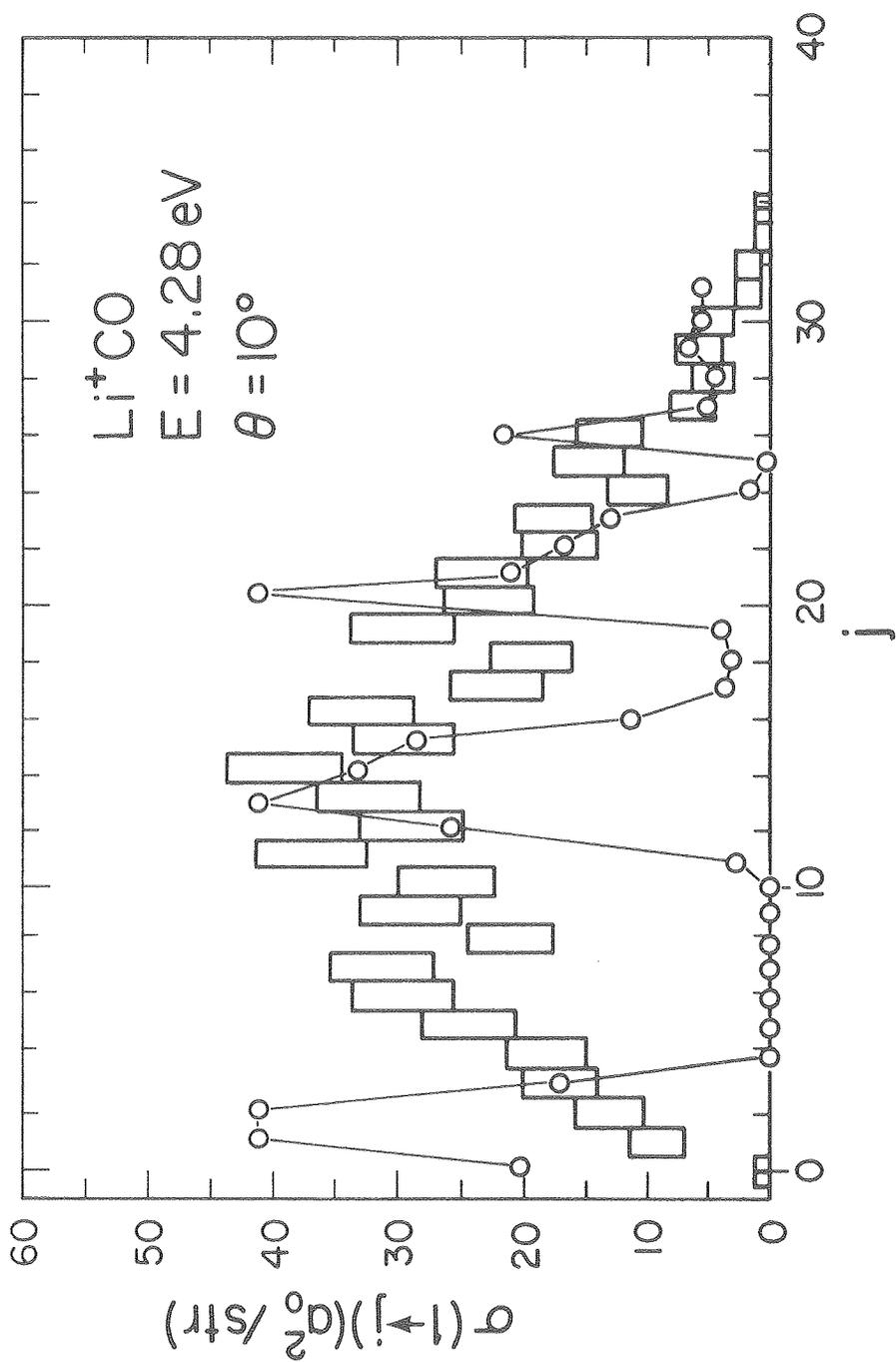
## Figure Captions

- Figure 1. Angular dependence of the  $\text{Li}^+ - \text{CO}$  potential energy surface at  $R = 3.0$  au. Shown are the Legendre polynomial expansions for 5, 7, 9, 11 and 13 terms.
- Figure 2. Differential cross sections for scattering at  $10^\circ$  and 4.28 eV relative kinetic energy. The boxes show the computed classical results and the circles the experimental results, scaled to the maximum in the computed values.



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Figure 1



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Figure 2

