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LOW ANGLE SCATTERING OF Li^+ by CO

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Abstract

Classical calculations are compared with experiment for the scattering of Li^+ ions by CO at 10° and 4.28 eV. Disagreement between the experimental and classical results is argued to be of quantum mechanical origin. CI calculations are reported for new points on the potential energy surface which demonstrate the need for further points.

It has been previously suggested [1] that rainbow structure found in the classical distribution of final rotational angular momentum of CO after collisions with Li^+ ions, is a possible explanation for apparently similar structure in the experimental time-of-flight (TOF) spectra [2] for this system. Recent low-angle scattering experiments [3] 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 been recently reported for K- N_2 and K-CO scattering by Schepper, Ross and Beck.[4,5] Their analysis of classical scattering from a rigid, hard-shell ellipsoid [4-6] also leads to a rotational rainbow explanation of the structure and gives a good qualitative description of their experiments. Rainbow structure has also been observed in the angular distributions of rotationally inelastic cross sections.[7-10] Additional theoretical work in this area has also recently appeared.[11-15]

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° - 50° , the classical trajectory results [1] are not in good agreement with the experiment.[2] The calculated distribution is considerably contracted compared to experiment. It has been demonstra-

ted that inclusion of the vibrational degree of freedom has little effect on this.[16]

The remaining most likely reasons for the discrepancies are i) the potential energy surface is not sufficiently accurate and ii) the system exhibits pronounced quantum mechanical interference effects. The present work indicates that while improvements to the surface are certainly possible and called for, quantum effects are actually the more likely reason.

Regarding the potential energy surface, it is unlikely 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. However, it is true that due to the anisotropy of the potential, particularly in the repulsive region, simply not enough points have been computed.

The angular dependence of the potential energy surface was expanded in Legendre polynomials of $\cos(\theta)$, where θ is the angle between the CO axis and the vector from the CO center of mass to the Li^+ ion. A 5 term expansion was used. For the high scattering angle study [1], the classical trajectories all had turning points in the region of $R = 3.0$ au, where R is the distance from 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. 16 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° - 50° 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° the turning points are around $R = 5.0$ which is in the potential well region where the anisotropy is weaker. The 5 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 156,000 trajectory study at 4.28 eV relative kinetic energy with CO initially in the $j = 1$ state. Trajectories were counted in a 1.5° interval centered at a scattering angle of 10° , 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.[3]

The classical distribution is seen to fall to zero more rapidly than the experimental one, but the effect is much less exaggerated than in the high angle comparison. [1] The experimental cross sections are also sharply structured in contrast to the classical ones. The classical cross sections do, however, show two sharp drops beginning at $j = 14$ and 22 . These are similar to the classical rainbow structures demonstrated in ref. 1, and their locations correspond well with the experimental peaks at $j = 13$ and 20 . The calculation cannot, however, account for the peaks at $j = 1$ and 26 .

It is also of interest to compute the TOF spectrum which would result from the classical cross sections. This is easily done by using the Gaussian line broadenings due to the finite resolution of the experimental apparatus.[3] This is shown in fig. 3. Also shown are the experimental TOF spectrum and two other computed spectra. One is computed from the "experimental" center-of-mass cross sections shown in fig. 2. The other, statistical distribution results from assuming that all energetically accessible states are equally probable. This results in constant CM cross sections but in a nearly elastically peaked TOF spectrum. All spectra have been normalized to unit maximum.

The statistical TOF spectrum has a shape similar to the gross features of the experiment but can not of course explain the peaks or the sharp decay for $j > 30$. These features are of dynamical origin.

The classical TOF spectrum shows hardly any structure at all. The structure in the CM cross sections is effectively washed out in the broadening by the apparatus. The classical peak at $j = 13$ is only discernable as a slight shift from the statistical peak. The structure at $j = 20$ shows up as a slight shoulder in the TOF spectrum.

Again, as in the high scattering angle study, we are faced with a fairly severe disagreement between the experimental and theoretical results. As to the question of whether this is due to quantum effects or an inadequate potential energy surface the evidence thus far indicates the former. As we have indicated above, the portion of the surface sampled in this study is very likely more accurate than that of the previous study. However, the chief reason for believing that quantum effects are at play here is the sharply structured CM cross sections which are necessary to reproduce the experimental TOF spectrum. While studies have shown that many features of the classical cross sections are sensitive to changes in the potential energy surface [1], in our experience it is difficult to imagine a reasonable surface which could produce the widely separated, sharply peaked structures deduced from the experiment. These are much more like what one would expect of an interference pattern. Confirmation or refutation of this must await a quantum mechanical study of the dynamics of this system.

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We are grateful to Dr. Richard Buss for several very useful discussions on the transformation from the center-of-mass to the laboratory frame of reference.

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

θ	$V(R,\theta)$
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

Figure Captions

Figure 1. Angular dependence of the Li^+ - 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° 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.

Figure 3. Time of flight spectrum for the scattering of Li^+ ions from CO at laboratory angle 8° and relative kinetic energy 4.28 eV. $\odot$ experimental points from ref. 3, - - - computed TOF spectrum from the classical cross sections, ——— computed TOF spectrum from the "best fit" cross sections of ref. 3, —.—.—, computed TOF spectrum from the statistical (constant) cross sections. The zero of the time scale is chosen to be the time of flight for elastic scattering at 0° . The scale above indicates the time of flight for energy losses corresponding to rotational transitions, Δj .

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Fig. 1

XBL 7911-5089

XBL 806-1125

Fig. 2

XBL806-1126

Fig. 3