Title

CROSSED MOLECULAR BEAM STUDIES ON THE INTERACTION POTENTIALS FOR Cl(2P) + Xe(IS)

Permalink

https://escholarship.org/uc/item/3fd9k3t4

Author

Becker, C.H.

Publication Date

1978-12-01

UC-4

Submitted to Chemical Physics Letters

LBL-8574 c.1
Preprint

CROSSED MOLECULAR BEAM STUDIES ON THE INTERACTION POTENTIALS FOR $Cl(^2P) + Xe(^1S)$

C. H. Becker, J. J. Valentini, P. Casavecchia,
S. J. Sibener and Y. T. Lee

December 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

LBL-8574 c.1

DISCLAIMER

LBL-8574

CROSSED MOLECULAR BEAM STUDIES ON THE INTERACTION POTENTIALS FOR $Cl(^2P) + Xe(^1S)$

C. H. Becker[a], J. J. Valentini[b], P. Casavecchia[c],
S. J. Sibener and Y. T. Lee[d]

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

December 1978

ABSTRACT

A crossed molecular beam experiment has been performed obtaining angular distributions of $^{35}Cl(^2P_{3/2,1/2})$ scattered off $Xe(^1S_0)$ at 4 nominal collision energies ranging from 2.37 to 26.1 kcal/mole. Interaction potential curves for the $X\frac{1}{2}$, $I\frac{3}{2}$, and $II\frac{1}{2}$ states are obtained via an approximate elastic scattering analysis as done previously for F - Xe, Kr, Ar, Ne. The $X\frac{1}{2}$ potential obtained (well depth $\varepsilon = 0.80$ kcal/mole, and minimum position $r_m = 3.23$ Å) is a corroboration of the recent spectroscopically derived potential of Sur et al.[2] The $I\frac{3}{2}$ interaction potential ($\varepsilon = 0.37$ kcal/mole, $r_m = 4.1$ Å) very closely resembles that of ground state Ar-Xe.

---

[a] Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

[b] Present address: Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, New Mexico 87545.

[c] Premanent address: Dipartimento di Chimica dell' Università, 06100 Perugia, Italy.

[d] Guggenheim Fellow, 1977-1978.

Introduction

There has been considerable interest recently in halogen-rare gas (X-RG) diatomics as they comprise a class of high power ultraviolet excimer lasers. Cl-Xe was one of the first of these lasing systems (at 308 nm) to be reported.[1] In fact, excimer is somewhat a misnomer for the Cl-Xe, and F-Xe, systems, as bound-bound spectral transitions are observed. This has allowed accurate spectroscopic (RKR) analysis of the ground state $X\frac{1}{2}$ Cl-Xe potential.[2] No spectroscopic information is available for the $I\frac{3}{2}$ or $II\frac{1}{2}$ states, though ab initio configuration interaction calculations have been performed on all of the states of possible laser interest.[3] The state labels used throughout are those appropriate to Hund's case c coupling, and the electronic states considered in this work are the $X\frac{1}{2}$ (or $I\frac{1}{2}$) and $I\frac{3}{2}$ arising from the ground state fourfold degenerate $^2P_{3/2} + {}^1S_0$ atomic asymptote, and the $II\frac{1}{2}$ from the doubly denerate spin orbit excited $^2P_{1/2} + {}^1S_0$ asymptote. Knowledge of all these states is helpful in understanding the presence or absence of lasing transitions and kinetic details of the laser medium.

Hence, as a check on the Cl-Xe spectroscopically derived $X\frac{1}{2}$ potential $V_{X\frac{1}{2}}$, to obtain chemically accurate information on the $V_{I\frac{3}{2}}$ and $V_{II\frac{1}{2}}$, and as an example of the usefulness of scattering studies in giving quantitative information on adiabatic potentials not readily accessible to spectroscopic analysis, a crossed molecular beam experiment has been performed on $Cl(^2P) + Xe(^1S)$.

Experimental

The apparatus and technique used has been described in detail elsewhere.[4] After two stages of differential pumping, the Cl and Xe supersonic beams cross at 90° under single collision conditions in the scattering chamber maintained at ~3 x 10^{-7} torr. The Xe beam was modulated at 150 Hz by a tuning fork chopper for background subtraction. A triply differentially pumped rotating quadrupole mass spectrometer with electron bombardment ionizer and ion counter recorded the angular distributions $I(\Theta)$ of ^{35}Cl scattered by Xe. Counting times went from 10 to 80 sec per point depending on the signal count rate, and signals at a reference angle were used for the comparison of the signals at all the observed angles in order to normalize possible fluctuations of beam intensities and other experimental conditions.

The stagnation pressure and temperature of the Xe beam was kept at 450 torr and 20°C. With a 0.1 mm nozzle, this is about the highest stagnation pressure for Xe without significant dimer formation in the expansion. Cl atoms were produced by Cl_2 thermal dissociation in a resistively heated high density graphite oven/nozzle.[5] Different relative collision energies E_{rel} were obtained by varying the Cl velocity utilyzing the seeded beam technique. The gas mixtures used were ~1% Cl_2 in He, Ar, or Xe, and stagnation pressures ~1000 torr were used. No XeCl or $XeCl_2$ was found in the hot beam. Beam velocities and spreads were measured by the time-of-flight method, and the full-width-at-half-maximum (FWHM) velocity spreads were ~20% for Cl and ~10% for Xe. FWHM angular divergences were about 1° for Cl and 2° for Xe.

The graphite oven temperature of ~2000°K produces about 21% spin orbit excited $^2P_{1/2}$ atoms; the spin orbit relaxation of Cl atoms is expected to be very slow during the isentropic expansion. Consequently the composition of Cl($^2P_{1/2}$) in the beam is not expected to differ from that in the oven. Some Cl_2 was also present in the beam and the small $^{35}Cl^+$ contribution from Cl_2 was taken into account from the measured angular distributions of Cl_2 detected as Cl_2^+ and the fragmentation ratio of $Cl_2(Cl^+/Cl_2^+)$ in the ionizer, and subtracted to give the final I(Θ) of Cl + Xe.

Inelastic scattering involving electronic transitions is expected to be a very small contribution to I(Θ) because of the large splitting of 881 cm^{-1} between $^2P_{1/2}$ and $^2P_{3/2}$ of Cl. Consequently no attempt was made to detect the fine structure inelastic process by time-of-flight.

Results and Analysis

Laboratory angular distributions of ^{35}Cl scattered off Xe are shown in Fig. 1 at nominal E_{rel} = 2.37, 2.57, 6.18, and 26.1 kcal/mole. Exemplary error bars are given, when visible outside the circles, representing ±1 standard deviation of the mean. The number of scans over an angular range varies from 3 to 9. As a check on the reproducibility of the data, the I(Θ) at E_{rel} = 2.57 kcal/mole was taken a considerable time after the other three I(Θ) were recorded using new beam set-ups intended for comparing I(Θ) at E_{rel} = 2.37. Although the collision energy turned out to be slightly higher, this data is compatible with the other I(Θ), as can be seen in Fig. 1.

An elastic scattering approximation is used in the analysis, which has been described elsewhere.[6] This method of computing differential cross sections neglects nonadiabatic coupling and is appropriate to molecules of Hund's case c coupling. JWKB phaseshifts are used in the single channel scattering. Twenty-one Newton diagrams contribute to final I(Θ) calculations to represent beam velocity spreads, and angular averaging is also performed to mimic the beam/detector geometry. Flexible piecewise analytic representations of the $V_{X\frac{1}{2},\, I\frac{3}{2}}$ are used and the approximation $V_{II\frac{1}{2}} \simeq V_{I\frac{3}{2}}$ is employed. The potential form is the Morse-Morse-Hermite-spline-van der Waals (MMHV) function:

$$
\begin{array}{rcllr}
f(x) & = & V/\varepsilon & x = r/r_m & (1) \\
f(x) & = & \exp(2\beta_1(1-x)) - 2\exp(\beta_1(1-x)) & 0 \leq x \leq 1 & \\
 & = & \exp(2\beta_2(1-x)) - 2\exp(\beta_2(1-x)) & 1 < x \leq x_1 & \\
 & = & a_1 + (x-x_1)\cdot\{a_2+(x-x_1)\cdot[a_3+a_4(x-x_1)]\} & x_1 < x < x_2 & \\
 & = & C_{6R}/x^6 - C_{8R}/x^8 & x_2 \leq x < \infty &
\end{array}
$$

where $C_{iR} = C_i/(\varepsilon r_m^i)$, and ε and r_m are the depth and position of the potential minimum. Conditions on the Hermite spline are continuity of $f(x)$ and $\frac{df(x)}{dx}$ at x_1 and x_2. The C_6 constants are estimated from the Slater-Kirkwood formula for effective number of electrons;[7] polarizability values are from the literature.[8,9] The C_6 of $I\frac{3}{2}$ corresponds to π symmetry, while the C_6 of $X\frac{1}{2}$ is best approximated by the average of the Σ and π contributions (see Ref. 10, Eq. (13)). The C_8 is estimated from the Ar-Xe C_8.[9] The permanent quadrupole-induced dipole R^{-8} induction term is neglected because of its small size, as are other coefficients of the asymptotic expansion.

The $V_{X\frac{1}{2},\ I\frac{3}{2}}$ are determined by fitting calculated I(Θ) to the experimental values through varying the analytic potential parameters. The C_6 and C_8 were held fixed though, and little variation was made in the x_1, x_2 values. Complete uniqueness of the fitted potentials is not guaranteed by this method. However, the range of the potentials are sensitive to the ratio of rainbow to wide angle scattering intensities. Rainbow and supernumerary rainbow positions and relative intensities are quite sensitive to potential well depths and curvature. To estimate these interaction potentials accurately it is necessary to measure the I(Θ) at several collision energies covering a wide range.

The validity of the elastic approximation is supported by its ability to corroborate an accurate spectroscopically determined $V_{X\frac{1}{2}}$ for F-Xe,[6a] and by more rigorous coupled-channel scattering calculations.[10]

The fitting began using an analytic representation of the spectroscopic numerical $V_{X\frac{1}{2}}$ values.[2a] It was found the experimental I(Θ) could not improve upon these values, so they were retained. Quite good sensitivity to the $V_{I\frac{3}{2}}$ well was found in the low energy I(Θ).

The final I(Θ) are shown in Fig. 1, the derived $V_{X\frac{1}{2},\ I\frac{3}{2}}$ are shown in Fig. 2, and the potential parameters are listed in Table I. As already noted, the $V_{II\frac{1}{2}}$ can be approximated by the $V_{I\frac{3}{2}}$. In general though, a better $V_{II\frac{1}{2}}$ can be derived as shown in Ref. 10 from the $V_{X\frac{1}{2}}$ and $V_{I\frac{3}{2}}$.

The resultant $V_{I\frac{3}{2}}$ shows very close resemblance to the ground state $^1\Sigma$ Ar-Xe potential. Elastic scattering studies performed in our laboratory have given the Ar-Xe potential, which we believe to be accurate to ±3%

in ε and r_m.[11] The parameters of the Ar-Xe potential are also listed in Table 1 for reference. This Ar-Xe potential is slightly outside other recently proposed values.[12]

Uncertainties in the Cl-Xe ε and r_m parameters are obtained by systematically varying the parameters and observing when the I(Θ) fits become poor. The estimated maximum uncertainites are within ±7% in ε and r_m for both the $V_{X\frac{1}{2}}$, $V_{I\frac{3}{2}}$. Possible errors in the Morse β parameters are likely to be of a similar magnitude, based on their observed influence on the I(Θ) during the fitting procedure. Sensitivity to the repulsive walls is less than for the well region owing to worse signal-to-noise for the structureless wide angle I(Θ), and multiple potential scattering. Of course, there is no information gained about the repulsive wall above the highest E_{rel}.

Discussion

The I(Θ) measured in this experiment is the result of scattering of Cl with Xe through three interaction potentials. For this type of scattering experiment involving multiple interaction potentials, it is not possible to carry out meaningful analysis of individual potentials unless experiments are performed at many collision energies covering a wide energy range, and the coupling between different states involved is weak (as in this case).

The application of the elastic approximation for Hund's case c coupling, as previously done for F-Xe[6a] and F-Ne, Ar, Kr,[6b] again is fruitful in its corroboration of the recently obtained spectroscopic

$V_{X\frac{1}{2}}$[2a] and its yielding an accurate $V_{I\frac{3}{2}}$ (and $V_{II\frac{1}{2}}$). The spectroscopic $V_{X\frac{1}{2}}$ was not determined to an absolute r_m, but rather to a value relative to two excited states, though sound arguments were used in estimating r_m. While this study cannot place an extremely tight bound on the $X\frac{1}{2}$ r_m, again, it is supportive of the conclusions of Sur et al. We consider all our stated uncertainties to be conservative.

The fact that the obtained $V_{I\frac{3}{2}}$ is so similar to the Ar-Xe ground state potential underlines the validity of the electronic closed shell-closed shell van der Waals picture where the interaction takes place with the fully occupied p orbital along the internuclear axis. The greater strength of this van der Waals interaction as compared to the F-rare gas series has allowed the most accurate $V_{I\frac{3}{2}}$ well determination to date, simply due to its significant influence on the three lowest E_{rel} $I(\Theta)$.

The common explanation for the Cl-Xe $V_{X\frac{1}{2}}$ consists of a combination of (a) less repulsion due to only a half-filled p orbital along the internuclear axis, (b) a small amount of charge transfer lessening this repulsion, and (c) the contribution from interatomic correlation energy[13] (the dispersion energy in the limit of zero electron overlap). As has been mentioned,[6b] it may also prove worthwhile to examine the approximation that the spin orbit coupling is constant over the range of internuclear distances considered. It appears that Cl-Xe and F-Xe are the only two significantly bound X-RG molecules. However, the shapes (or force constants) of these two $V_{X\frac{1}{2}}$ are very different, F-Xe having a very tight well and Cl-Xe being broad. At this point, an explanation of this phenomenon seems possible only by considering the absolute strengths of the above mentioned contributions as a function of internuclear distances.

Nonadiabatic coupling in XeCl and its influence on scattering is discussed in Ref. 10.

Finally, if there is a desire to extrapolate these repulsive walls to higher energy, one may make use ab initio calculations,[3] at least in obtaining the wall slopes. Alternatively, one may make use of the simple model recently proposed[14] to obtain Born-Mayer repulsion parameters from values of ε, r_m, and van der Waals coefficients, especially for the $V_{I\frac{3}{2}}$ and $V_{II\frac{1}{2}}$.

Acknowledgement

We thank J. Tellinghuisen for communicating his results prior to publication. This work was supported by the Office of Naval Research (Contract No. N14-77-C-0101), and by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. P. C. acknowledges a fellowship from the Italian National Research Council (CNR).

References

1. J. J. Ewing and C. A. Brau, Appl. Phys. Lett. 27, 350 (1975).
2. (a) A. Sur, A. K. Hui, and J. Tellinghuisen, (to appear in J. Mol. Spectr.); (b) J. Tellinghuisen, J. M. Hoffman, G. C. Tisone, and A. K. Hays, J. Chem. Phys. 64, 2484 (1976).
3. P. J. Hay and T. H. Dunning, Jr., J. Chem. Phys. 69, 2209 (1978).
4. P. E. Siska, J. M. Parson, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. 55, 5762 (1971); Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, Rev. Sci. Instr. 40, 1402 (1969).
5. J. J. Valentini, M. J. Coggiola, and Y. T. Lee, Rev. Sci. Instr. 48, 58 (1977).
6. (a) C. H. Becker, P. Casavecchia, and Y. T. Lee, J. Chem. Phys. 69, 2377 (1978); (b) C. H. Becker, P. Casavecchia, and Y. T. Lee (submitted to J. Chem. Phys.).
7. K. S. Pitzer, Adv. Chem. Phys. 2, 59 (1959).
8. E. A. Reinsch and W. Meyer, Phys. Rev. A 14, 915 (1976).
9. J. S. Cohen and R. T. Pack, J. Chem. Phys. 61, 2372 (1974).
10. C. H. Becker, P. Casavecchia, Y. T. Lee, R. E. Olson, and W. A. Lester, Jr. (to be submitted to J. Chem. Phys.).
11. C. H. Becker, R. J. Buss, and Y. T. Lee, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Annual Reports 1977 (LBL-7355), pp. 384-386.
12. G. C. Maitland and W. A. Wakeham, Mol. Phys. 35, 1443 (1978).
13. M. Krauss and B. Liu, Chem. Phys. Lett. 44, 257 (1976).
14. K. T. Tang and J. P. Toennies, J. Chem. Phys. 66, 1496 (1977); errata, ibid., 67, 375 (1977) and 68, 786 (1978).

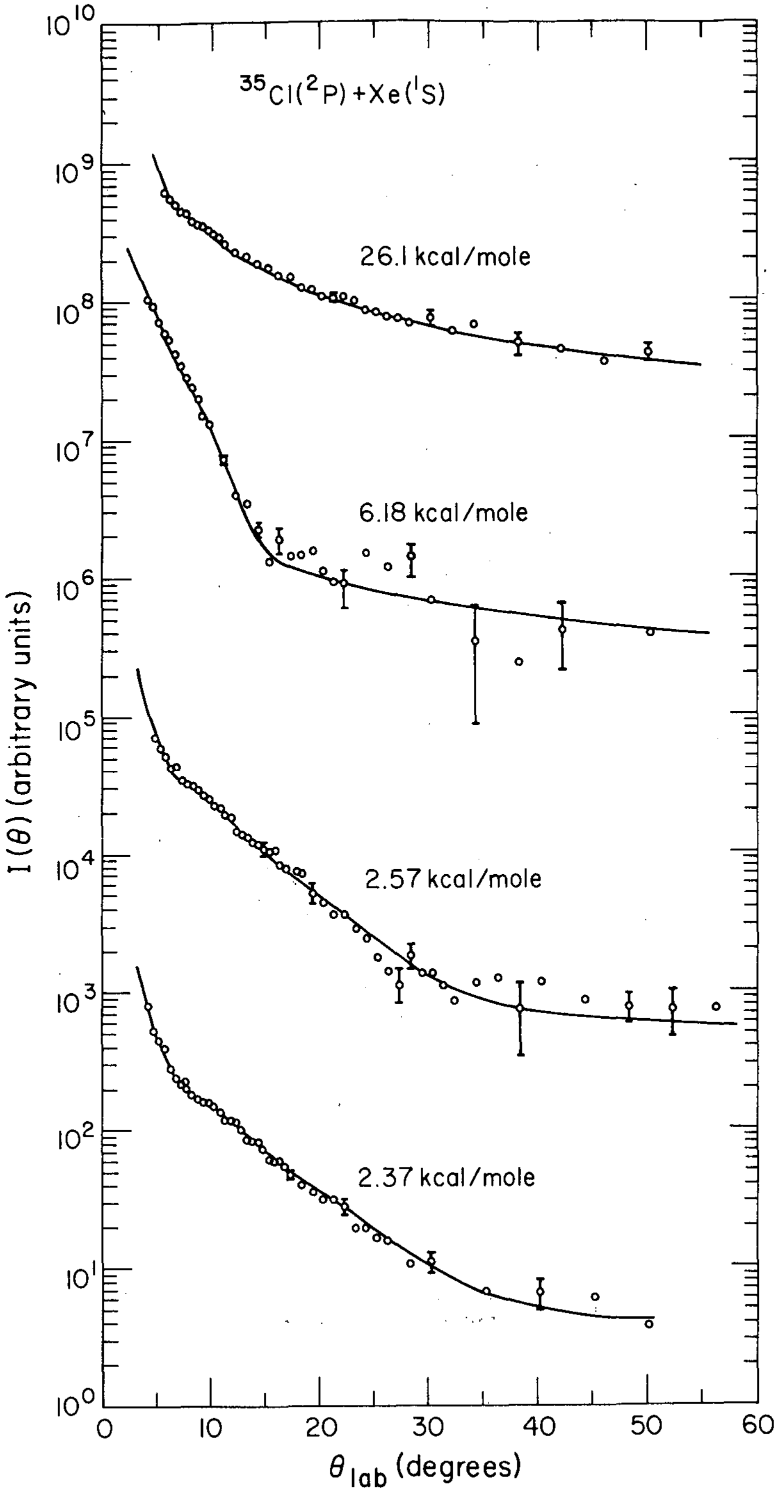
Table 1. Cl-Xe $X\frac{1}{2}$, $I\frac{3}{2}$ and Ar-Xe $^1\Sigma$ Interaction Potential Parameters

	XeCl, $X\frac{1}{2}$	XeCl, $I\frac{3}{2}$	Ar + Xe
ε (kcal/mole)	0.80	0.37	0.379
r_m (Å)	3.23	4.10	4.01
β_1	5.2	7.6	6.5
β_2	3.3	5.1	6.33
C_6 (kcal/mole · Å^6)	2279.	2410.	1957.
C_8 (kcal/mole · Å^8)	14250.	14250.	12005.
C_{10} (kcal/mole · Å^{10})	---	---	93502.
x_1	1.2100	1.1162	1.1088
x_2	1.6500	1.3500	1.4500
a_1	-0.7500	-0.8000	-0.7519
a_2	1.6500	2.5216	3.1665
a_3	0.4434	2.0941	-5.5247
a_4	-2.5063	-13.6316	3.8055

Figure Captions

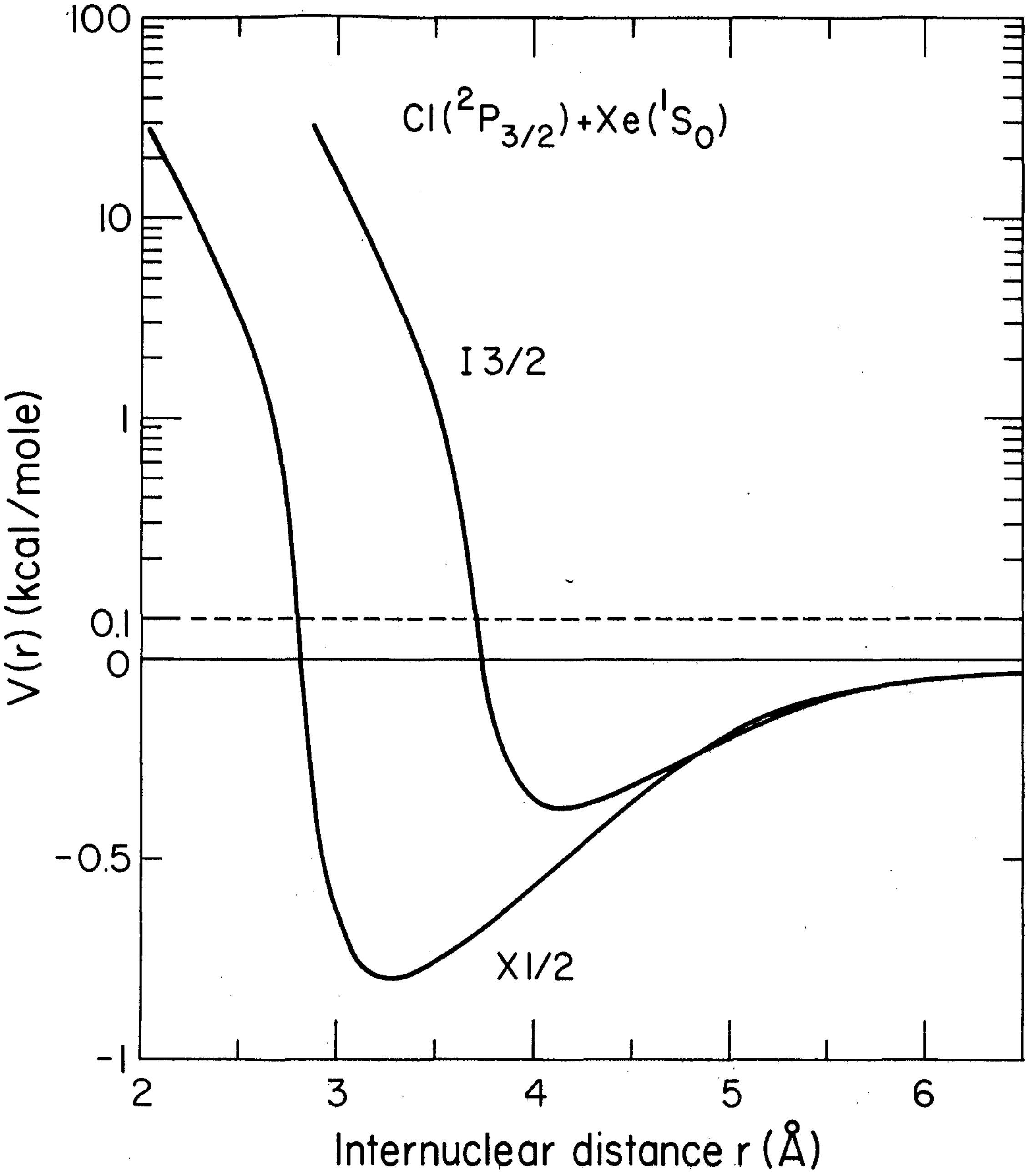
Fig. 1. Experimental number density angular distributions of ^{35}Cl scattered off Xe (circles), and best fit calculation (solid line) using the potential parameters of Table 1. Representative error bars are ±1 standard deviation of the mean.

Fig. 2. Cl Xe $X\frac{1}{2}$ and $I\frac{3}{2}$ interaction potentials. Note scale change at 0.1 kcal/mole.



XBL 7811-12585

Fig. 1



XBL 7811-12584

Fig. 2

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720