

FIG. 1. Pressure-induced shifts of lines in the 2-0 band of HCl due to xenon; at four temperatures.

cell length was 30 cm for the observations at -77°C and 50 cm for the others. The procedure for measuring the shifts was similar to that already described.³ The reference cell contained a small quantity of HCl only, and was at room temperature. The results are presented in the figure as shifts for a constant density of xenon.

In impact theories,⁴ collisions with an impact parameter smaller than a certain critical value b_0 are treated as "strong." While affecting linewidth, these strong collisions do not contribute to the shift.

If it is assumed that the interaction energy is proportional to the inverse sixth power of the intermolecular distance, impact theories suggest that for lines with small J numbers, for which b_0 can be shown to be large, the shift should be proportional to $T^{3/10}$.

For high values of J , b_0 can be shown to be smaller, and a statistical factor arising from the intermolecular potential may play an important role. This factor favors closer collisions, leading to larger shifts, but since it decreases in importance with increasing temperature, it may be the cause of the reversal, at high J numbers, of the direction of the temperature dependence that seems to be apparent in Fig. 1.

¹ M. A. Hirshfeld, J. H. Jaffe, and S. Kimel, *J. Chem. Phys.* **32**, 297 (1960); D. H. Rank, W. B. Birtley, D. P. Eastman, and T. A. Wiggins, *ibid.* **32**, 296 (1960); **33**, 323 (1960). A. Ben-Reuven, S. Kimel, M. A. Hirshfeld, and J. H. Jaffe, *ibid.* **35**, 955 (1961).

Papers read by D. H. Rank and by S. Kimel at the International Conference on Spectral Line Shape and Molecular Interactions Rehovoth, August 1961.

² Papers read by H. Margenau, by R. Herman, by A. D. Buckingham,¹ by R. Englman, and A. Ben-Reuven at the Rehovoth Conference.

³ S. Kimel, M. A. Hirshfeld, and J. H. Jaffe, *J. Chem. Phys.* **31**, 81 (1959).

⁴ P. W. Anderson, *Phys. Revs.* **76**, 647 (1949); C. J. Tsao and B. Curnutte, Geophysical Research Paper No. 69 (U. S. Air Force Cambridge Research Lab.) 1960.

Evaluation of the Intermolecular Potential Well Depth from Observations of Rainbow Scattering: Cs-Hg and K-Hg*

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THE present communication reports measurements of rainbow scattering for the Cs-Hg and K-Hg systems, from which the depths of the intermolecular potentials ϵ_{12} may be directly evaluated.

Mason¹ has presented a classical theoretical analysis of molecular beam scattering in which he pointed out the possibility of observing a discontinuity in the angular distribution at a critical deflection angle χ_s , since termed² the rainbow angle θ_r . This angle corresponds to the trajectory exhibiting maximum attraction between the interacting particles, i.e., θ_r is the minimum of the deflection function $\Theta(b^*)$. Since θ_r is strongly dependent upon the reduced relative collision energy $K = \frac{1}{2}\mu v_r^2/\epsilon_{12}$, its location may be used to determine ϵ_{12} directly.

The experiments were carried out using velocity selected alkali beams scattered by a crossed, collimated Hg beam. The apparatus has been briefly described³; the velocity resolution of the selector was 4.7%; only a small additional spread in relative speed v_r is introduced by the thermal distribution in the Hg beam. The scattering angles and intensities have been corrected to the center of mass (c.m.) system, taking cognizance of the (average) Hg speed. Absolute cross sections

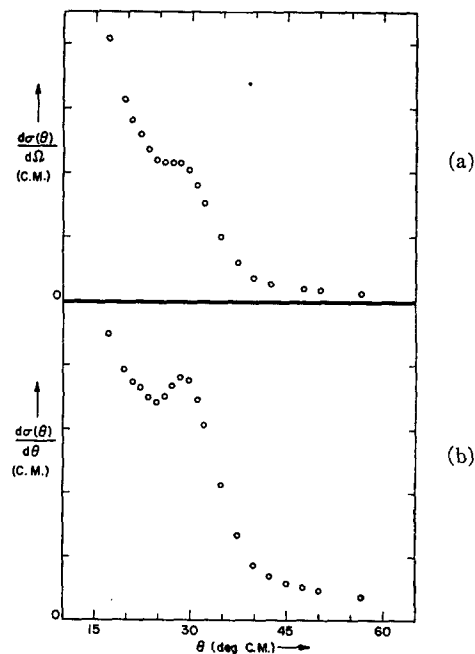


FIG. 1. (a). Example of rainbow scattering (observations corrected to the c.m. system. K-Hg, $v_r=1026$ m/sec). (b) Alternate representation of the same data (see text).

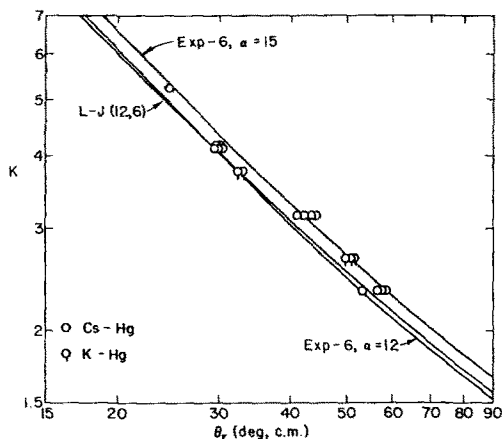


FIG. 2. Energy dependence of θ_r . Solid lines: calculated, for indicated potential functions. Points: experimental, assuming $\epsilon/k=555^\circ\text{K}$.

are not required for the present application; thus the vertical scales in Fig. 1 are arbitrary.

Figure 1(a) is an example of the differential elastic solid angle scattering cross section $d\sigma(\theta)/d\Omega$, for K-Hg at $v_r=1026$ m/sec, while Fig. 1(b) shows the corresponding differential polar scattering cross section $d\sigma(\theta)/d\theta=2\pi\sin\theta d\sigma(\theta)/d\Omega$; analogous results⁴ were obtained for Cs-Hg. θ_r was taken to be the inflection point on the rapidly falling portion of $d\sigma(\theta)/d\Omega$ after the "bump."

Figure 2 shows calculated curves of θ_r vs K for the Lennard-Jones (12,6)⁵ and the exp-6⁶ potential functions. The experimental points are superimposed; the ordinates have been fitted assuming $\epsilon_{12}/k=555^\circ\text{K}$ for both the Cs-Hg and K-Hg systems. Over the range studied, a given fractional uncertainty in θ_r leads to nearly the same fractional error in the derived ϵ_{12} . It can also be seen (Fig. 2) that the value obtained for ϵ_{12} is quite insensitive to the steepness assumed for the repulsion.

Without velocity selection the Maxwellian angular distributions show no evidence of rainbow scattering and indeed, over the angular range of the present study (5–80° C.M.), may be fitted with an extremely wide range of ϵ_{12} values.⁸

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¹ E. A. Mason, *J. Chem. Phys.* **26**, 667 (1957).

² K. W. Ford and J. A. Wheeler, *Ann. Phys. (N. Y.)* **7**, 287 (1959).

³ H. U. Hostettler and R. B. Bernstein, *Phys. Rev. Letters* **5**, 318 (1960).

⁴ Rainbow scattering has also been observed by D. Beck, E. F. Greene, and J. Ross for K—Kr and K—HBr [E. F. Greene (private communication)].

⁵ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

⁶ cf. H. Pauly, *Z. Naturforsch.* **14a**, 1083 (1959).

Comments and Errata

Erratum: Normal Vibrations of the Polymer Molecules of Helical Configuration. II. A Simple Method of Factoring of the Secular Equation

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IN Eq. (9), page 1052, for "sin3k ω " in the matrix elements of the 1st row 3rd column, 2nd row 4th column, 3rd row 1st column, and 4th row 2nd column, read "sin2k ω ".

Notes

Observations in Proton NMR Spectra of Long-Range Coupling Between Protons and Carbon-13 in Natural Abundance

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THE effects of short-range coupling between protons and carbon-13 have been observable with available equipment for a number of years. The long-range coupling can now be observed in many compounds despite the difficulties imposed (1) by the low (about 1.1%) natural abundance of C¹³, and (2) by the rather low coupling constants of 5–10 cps. This coupling may be measured directly in the proton spectrum whenever the principal central peak of the uncoupled protons is sufficiently narrow (see Table I) of the order of 1½ cps. These observations were made with an unmodified A-60 NMR spectrometer manufactured by Varian Associates with sample spinning frequencies of about 35 cps.

TABLE I. Observations on long-range coupling between protons and carbon-13 in natural abundance.

Compound	Proton species	J (long C ¹³ —H ¹)
acetonitrile		9.8–10.0
sodium acetate		5.8–6.0
methyl acetate	acetate	6.8–6.9
acetophenone	methyl	5.7
acetaldehyde	methyl	6.0
toluene	methyl	5 (broad)