PHYSICAL REVIEW LETTERS

VOLUME 16 7 MARCH 1966 NUMBER 10

LONG-RANGE INTERATOMIC FORCES FROM PREDISSOCIATION DATA AND RESONANCES IN ATOMIC SCATTERING*

Richard B. Bernstein

Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin

(Received 17 January 1966)

There has been a recent renewal of interest in the experimental determination of long-range interatomic forces and their comparison with theory. Although the most direct route has been via absolute cross sections for elastic scattering of atomic beams at thermal energies,[1] a large body of existing predissociation data represents another substantial source of relevant information, not yet fully exploited. In what follows we develop the explicit relationships needed to make use of the limiting curve of dissociation[2] (LCD) for the determination of long-range interatomic forces from spectra.[2-7] We also establish the close connection between the LCD and the expected pattern of resonances[8] (inverse predissociation) in atom-atom scattering cross sections. The relationships become especially simple in view of the fact that the position and height of the centrifugal barrier in the effective potential are determined primarily by the long-range part of the interaction.

For any potential $V(r)$ with an attractive well, the maximum of the effective potential $V_{\mathrm{eff}}(r,j) \equiv V(r)+j(j+1)\hbar^2/2\mu r^2$ is given by

$$V_{\mathrm{eff}}(r_{\mathrm{max}}) = V(r_{\mathrm{max}}) + \tfrac{1}{2} r_{\mathrm{max}} V'(r_{\mathrm{max}}), \tag{1}$$

where the position of the maximum, r_{max}, is determined by

$$r_{\mathrm{max}}^{\;3} V'(r_{\mathrm{max}}) = (\hbar^2/\mu) j(j+1). \tag{2}$$

Here j is the rotational quantum number, μ the reduced mass, and $V'(r_{\mathrm{max}}) = (dV/dr)_{r=r_{\mathrm{max}}}$. For a potential whose long-range behavior can be expressed by $V(r) \sim -C_n r^{-n}$, the effective potential may be approximated, for the situation where $r_{\mathrm{max}} \gtrsim 1.5 r_e$ (the equilibrium internuclear separation), by

$$V_{\mathrm{eff}}(r) \cong -C_n r^{-n} + \hbar^2 j(j+1)/2\mu r^2, \tag{3}$$

so that Eq. (2) simplifies to

$$r_{\mathrm{max}}(j) \cong \left[\frac{n\mu C_n}{\hbar^2 j(j+1)}\right]^{1/(n-2)}. \tag{4}$$

Substitution of relations (2) and (4) into Eq. (1) yields an explicit equation for the LCD (the "breaking-off curve"), i.e., for E_{LCD} in cm^{-1}:

$$E_{\mathrm{LCD}} = E_0 + (hc)^{-1} V_{\mathrm{eff}}(r_{\mathrm{max}}) \cong E_0 + S_n [j(j+1)]^{n/(n-2)}, \tag{5}$$

where

$$S_n = \frac{n-2}{4\pi c}\left[\frac{\hbar^{n+2}}{(n\mu)^n \cdot C_n^{\;2}}\right]^{1/(n-2)} (\mathrm{cm}^{-1}), \tag{6}$$

and E_0 is the term corresponding to the dissociation limit. For the important case[9] of $n=6$,

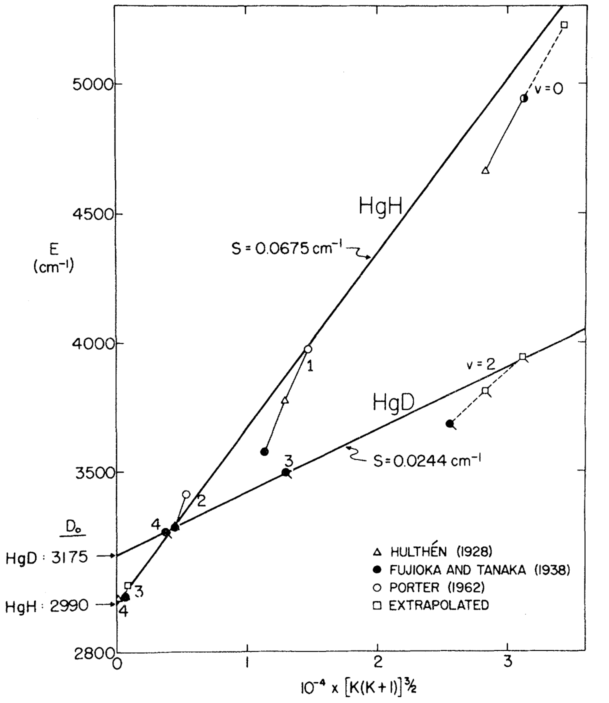

FIG. 1. Plots of last unpredissociated F_1 terms of HgH and HgD ($X\,^2\Sigma^+$). The intercepts of the straight lines yield the indicated (±5 cm^{-1}) dissociation energies (and thus the well depth $D_e = 3660 \pm 10$ cm^{-1}). Slopes yield the long-range constant $C_6 = 3.0 \times 10^{-59}$ erg cm^6 (same for both molecules).

for which E_{LCD} is linear in $[j(j+1)]^{3/2}$, one obtains

$$C_6(\text{erg cm}^6) = 1.411\times 10^{-61}/\mu_A{}^3 s_6{}^2 \qquad (\mu_A \text{ in amu}). \tag{7}$$

The above relations are illustrated in Figs. 1 and 2(a) for the $X\,^2\Sigma^+$ state of HgH and HgD.[10] The resulting C_6 constants [using Eq. (7)] are $(3.0_7$ and $2.9_9)\times 10^{-59}$ erg cm^6 for HgH and HgD, respectively (identical, within the uncertainty of ca. 10%). For comparison, using the Slater-Kirkwood approximation, we predict[11] the value $C_6 = 3.5\times 10^{-59}$ erg cm^6.

One of the first LCD studies was the predissociation of the $C\,^3\Pi_u$ state of N_2 (see Büttenbender and Herzberg[3] and Coster, Van Dijk, and Lameris[12]). Recently, it has been suggested[13] that a $^5\Pi_u$ state is responsible for the predissociation; in any case it is probable that the products of dissociation are $N(^4S) + N(^2D)$. Figure 2(b) is a plot of the data of Büttenbender and Herzberg[3] (first predissociated levels) from which $s_6 = 2.8\times 10^{-3}$ cm^{-1} and thus a value of $C_6 = 5.2\times 10^{-59}$ erg cm^6 is obtained.

Another early example is the predissociation of the $b\,^3\Sigma^+$ state of CO (see Schmid and Gerö, Ref. 4); this state dissociates to $C(^3P)$ and $O(^3P)$. According to Knipp[14] the long-range interac-

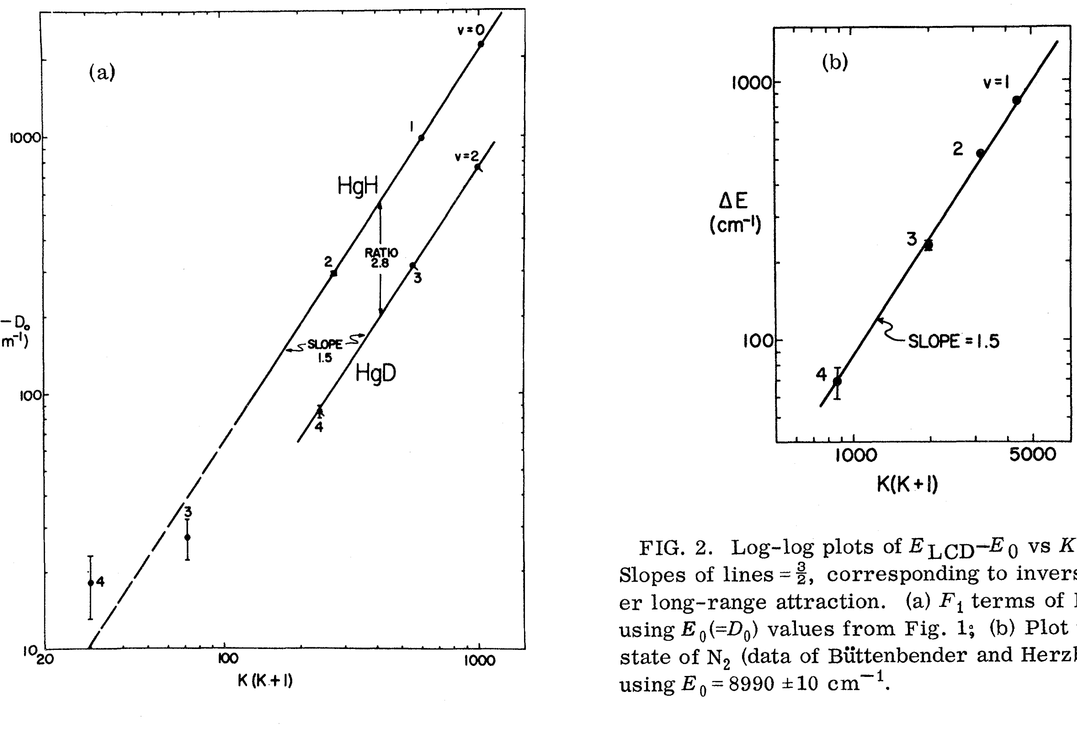

FIG. 2. Log-log plots of $E_{\text{LCD}} - E_0$ vs $K(K+1)$. Slopes of lines $= \frac{3}{2}$, corresponding to inverse sixth power long-range attraction. (a) F_1 terms of HgH and HgD, using $E_0(=D_0)$ values from Fig. 1; (b) Plot for $C\,^3\Pi_u$ state of N_2 (data of Büttenbender and Herzberg, Ref. 3), using $E_0 = 8990 \pm 10$ cm^{-1}.

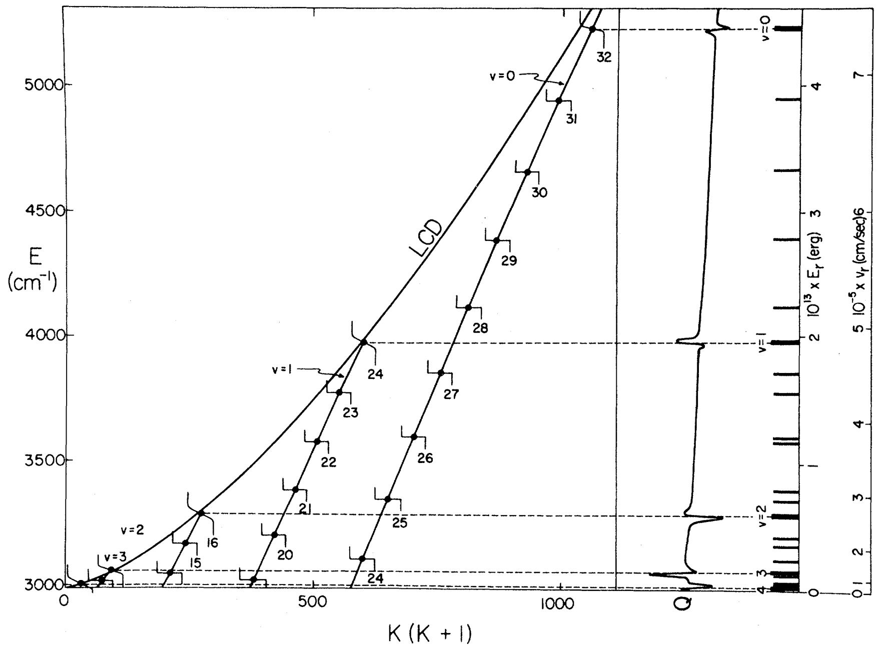

FIG. 3. Composite LCD and resonance plot for HgH. Left-hand side: unpredissociated F_1 terms, computed from spectroscopic constants of Fujioka, Ref. 10; indices are K values. The LCD is that from Fig. 1. Right-hand side: spectrum of the quasibound states; "sharp" levels characterized by abrupt rise in phase shift by π, "broad" levels by sigmoid $d\eta/dE_r$ at resonance (phase shift changes shown schematically). $Q(E_r)$ represents (schematically) the expected appearance of the resonance scattering pattern (v_r is the relative collision velocity).

tion of two non-S-state atoms is predominantly quadrupole-quadrupole, yielding $V\cong -C_5r^{-5}$. With this assumption, making use of the breaking-off data (see Schmid and Gerö, Ref. 4) ($j\cong 43$ at 89 820 cm^{-1}) and taking $D_0(\text{CO})=89\,620\pm 20$ cm^{-1} (see Gaydon, Ref. 3), one obtains $s_5=6.7\times10^{-4}$ cm^{-1} and thus an experimentally derived value of $C_5=2.0\times10^{-51}$ erg cm^5 (to be compared with Knipp's predicted value[14] of $3.0_7\times10^{-51}$ erg cm^5). This appears to be the first experimental determination of a C_5 interaction; more detailed analyses of this and other[15] analogous predissociations are suggested.

The same factors responsible for the line broadening and breaking off of the rotational structure (i.e., tunneling penetration and surmounting of the centrifugal barrier) lead to resonance behavior in elastic atomic scattering (inverse predissociation). The spectrum of the quasibound (virtual) states of positive energy is reflected in the pattern of resonances (see Bernstein et al.,[8] and Buckingham, Fox and Gal[16]) in the scattering cross section $Q(E_r)$, where $E_r=\frac{1}{2}\mu v_r^2$ is the relative kinetic energy. However, only for the states of short lifetime [i.e., the broadened levels near the maximum in $V_{\text{eff}}(r,j)$] will the resonance widths $\Gamma_{j,v}$ be sufficient to allow observation of the resonances in Q with presently available velocity resolution. These are just the levels too broad for observation in the predissociation spectrum. Thus the resonance pattern should be rather simple, and governed by the predissociation terms, as illustrated in Fig. 3 (with suitable indexing of the levels). From such a resonance pattern the LCD and thus the constant C_n can be obtained; from the mean thermal cross section ($\bar{Q}$) the constant C_n can be independently estimated,[1] thus permitting a highly desirable redundancy in the determination of the long-range interatomic force.

The author wishes to thank Dr. C. F. Curtiss, Dr. J. W. Fox, Dr. G. Herzberg, Dr. J. O. Hirschfelder, and Dr. H. S. Taylor for valuable comments and discussions.

---

*Work supported by the National Aeronautics and Space Administration Grant No. NsG-275-62.

[1] See, e.g., R. B. Bernstein in Atomic Collision Processes, edited by M. R. C. McDowell (North-Holland

Publishing Company, Amsterdam, 1964), p. 895; H. Pauly and J. P. Toennies in Advances in Atomic and Molecular Physics, edited by D. R. Bates and I. Esterman (Academic Press, Inc., New York, 1965), Vol. 1, p. 201; E. W. Rothe and R. H. Neynaber, J. Chem. Phys. 43, 4177 (1965).

[2] Since its introduction by Herzberg[3] more than 30 years ago, the construct of the LCD has been widely used by spectroscopists to extract information about the potential energy curve of a predissociating (Pr) state. By extrapolation of the plot of E_{LCD} vs j^2+j to zero j, the dissociation limit of the Pr electronic state is obtained[4]; the existence, height, and position of a potential hill for the Pr state can be deduced (for the case of a linear LCD)[5]; point-wise construction of the outer branch of $V(r)$ for the Pr state has been possible[6]; more recently, from the shape of the LCD, inferences have been drawn about the electronic states of the atomic dissociation products[7]; in the case of H_2, quantitative estimates have been made of the potential curve of the $B'\,{}^1\Sigma_u{}^+$ state in the vicinity of its dissociation limit.[7]

[3] G. Büttenbender and G. Herzberg, Ann. Phys. (N.Y.) 21, 577 (1934-1935); R. Schmid and L. Gerö, Z. Physik 104, 724 (1937); see also R. S. Mulliken, Phys. Rev. 25, 509 (1925); O. Oldenberg, Z. Physik 56, 563 (1929); R. de L. Kronig, Z. Physik 62, 300 (1930); D. S. Villars and E. U. Condon, Phys. Rev. 35, 1028 (1930); G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950); A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules (Dover Publications, New York, 1950).

[4] See Büttenbender and Herzberg, Schmid and Gerö, Herzberg, and Gaydon, Ref. 3; see also, e.g., R. Schmid and L. Gerö, Z. Physik 96, 198 (1935); R. Schmid, Physik. Z. 37, 55 (1963); and, for a recent example, G. Herzberg and A. Monfils, J. Mol. Spectry. 5, 482 (1960).

[5] G. Herzberg, J. Phys. Chem. 41, 299 (1937); G. Herzberg and L. G. Mundie, J. Chem. Phys. 8, 263 (1940).

[6] See Schmid and Gerö, Ref. 3; for a recent case see T. Namioka, J. Chem. Phys. 43, 1636 (1965).

[7] See Herzberg and Monfils, Ref. 4; see also Namioka, Ref. 6.

[8] K. W. Ford, D. L. Hill, M. Wakano, and J. A. Wheeler, Ann. Phys. (N.Y.) 7, 239 (1959); S. Imam-Rahajoe, C. F. Curtiss, and R. B. Bernstein, J. Chem. Phys. 42, 530 (1965); R. Düren, R. Helbing, and H. Pauly, Z. Physik 188, 468 (1965); B. C. Eu and J. Ross, to be published; R. B. Bernstein, C. F. Curtiss, S. Imam-Rahajoe, and H. T. Wood, to be published.

[9] For $n=5$, $C_5(\mathrm{erg\ cm}^5)=4.312\times10^{-54}/\mu_A{}^{5/2}S_5{}^{3/2}$; etc.

[10] The data are principally those of Y. Fujioka and Y. Tanaka, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 34, 713 (1938). HgH is Hund's case b; the upper of the ${}^2\Sigma^+$ doublet is designated F_1, for which $j=K+\frac{1}{2}$. See also E. Hulthén, Z. Physik 50, 319 (1928); T. L. Porter, J. Opt. Soc. Am. 52, 1201 (1962).

[11] Calculated using the standard S-K equation with $\alpha_{\mathrm{H}}\cong\alpha_{\mathrm{D}}=0.67\ \mathrm{\AA}^3$, $\alpha_{\mathrm{Hg}}=51\ \mathrm{\AA}^3$; $N_{\mathrm{H}}=N_{\mathrm{D}}=1$, $N_{\mathrm{Hg}}=2$.

[12] D. Coster, E. W. Van Dijk, and A. J. Lameris, Physica 2, 267 (1935).

[13] P. K. Carroll, Proc. Roy. Soc. (London) A272, 270 (1963); F. R. Gilmore, J. Quant. Spectr. Radiative Transfer 5, 369 (1965); P. K. Carroll and R. S. Mulliken, J. Chem. Phys. 43, 2170 (1965).

[14] J. Knipp, Phys. Rev. 53, 734 (1938).

[15] Of particular interest would be those for a state which dissociates to a pair of identical atoms in S and P (or P and D) states, for which the resonant dipole-dipole interaction [G. W. King and J. H. Van Vleck, Phys. Rev. 55, 1165 (1939)] $V\sim-C_3r^{-3}$ would yield an LCD with $\Delta E\propto[j(j+1)]^3$.

[16] See R. A. Buckingham, J. W. Fox, and E. Gal, Proc. Roy. Soc. (London) A284, 237 (1965) for a phase-shift analysis of the resonances in the $X\,{}^1\Sigma_g{}^+$ state of H_2. If one plots their resonance energies versus $j(j+1)$ as in Fig. 3 the lines for $v=0,\cdots,13$ are nearly straight as expected, and the resulting LCD exhibits directly the substantial dipole-quadrupole (r^{-8}) contribution to the long-range interaction.