UNCLASSIFIED

AD 400 319

Reproduced
by the

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA

UNCLASSIFIED

AFCRL - 63 - 430

<div dir="rtl">מכון ויצמן למדע</div>

THE WEIZMANN INSTITUTE OF SCIENCE

REHOVOTH, ISRAEL

Best
Available
Copy

ANNUAL SUMMARY REPORT NO. 2

Contract No. AF 61(052)-388

Signature of Principal Investigator

....

J.H. Jaffe

The Weizmann Institute of Science, Rehovoth, Israel

February, 1963

THEORY OF PRESSURE-INDUCED SHIFTS OF
INFRARED LINES*

A. Ben-Reuven**, H. Friedmann***, and J.H. Jaffe

The Weizmann Institute of Science, Rehovoth, Israel

ABSTRACT

A treatment is presented that accounts to a large extent for the j-dependence of pressure induced shifts due to noble gases of lines in HCl bands. After a brief critical review of the theoretical work done on this subject to date, an improved phase-shift approximation for the intermolecular collision process is worked out with a coordinate system fixed in space during the collision. The main features of the observed phenomena are accounted for using only parameters calculated directly from known molecular properties. A discussion of the limitations of this theory is given. It appears that in order to achieve further improvement, the finite probability of j-transitions and the influence of short-range forces should be taken into account.

INTRODUCTORY REVIEW

1a

The subject of this paper is the theoretical interpretation
of pressure-induced shifts of lines in the vibration-rotation absorption
bands of gaseous HCl pressurized by noble gases, about which there
is now a large body of experimental data,[1-5] The most interesting

1. M.A. Hirshfeld, J.H. Jaffe, and S. Kimel, J. Chem. Phys. 32, 297 (1960).

2. D.H. Rank, W.B. Birtley, D.P. Eastman, and T.A. Wiggins, J. Chem. Phys.
   32, 296 (1960); 33, 323, 327 (1960).

3. A. Ben-Reuven, S. Kimel, M.A. Hirshfeld, and J.H. Jaffe, J. Chem. Phys.
   35, 955 (1961), referred to hereafter as I.

4. J.H. Jaffe, A. Landau, and A. Ben-Reuven, J. Chem. Phys. 36, 1946 (1962).

5. D.H. Rank, Office of Naval Research, Technical Report for the period
   June 1 1961 - June 1 1962.

feature of these shifts, and the most difficult one to account
for theoretically, is their dependence upon the rotational
quantum number j : individual rotational lines of a band are each
shifted differently, most of them towards lower frequencies.
Generally the shifts increase on passing from the lighter helium
to the heavier xenon as the perturbing agency, and from the 1-0
band to the 2-0 band of HCl. The observed shifts vary from about

* is presented,

1.

$10^{-3} cm^{-1}$ per standard atmosphere of helium in the 1-0 band to about $10^{-1} cm^{-1}$ per standard atmosphere of xenon in the wings of the 2-0 band.

The many attempts that have been made to explain the observed phenomena have met with only partial success. In some treatments a static approach was adopted where the perturbation of the polar HCl molecule was attributed to an assembly of noble gas atoms statically distributed around it.[6-8]

---

6. A.D. Buckingham, Trans. Faraday Soc. 58, 449 (1961).

7. H. Margenau, papers read at the International Conference on Spectral Line Shape and Molecular Interactions, Rehovoth, Aug. 1962, and at the Symposium on Effects of Intermolecular Forces on Intramolecular Properties, Toronto, Jan. 1962.

8. H. Margenau and H.C. Jacobson, to be published.

Other attempts were based on an impact approximation where it is assumed that those collisions which affect appreciably the states of the absorbing molecules by shifting their phases or by causing transitions, are of short duration compared with the time interval

between two successive collisions.[9-11] In all these theories

9. R. Engleman, J. Chem. Phys. 36, 3127 (1962).
10. P. Schofler, and B. Oksengorn, Molecular Phys. 5, 473 (1962).
11. R.M. Herman, to be published.

the translational motion of the molecules is treated classically.

Fig. 1a depicts a noble gas atom in the neighborhood of a diatomic molecule. Because of the spherical symmetry of the noble gas atom, the interaction energy V depends on one angle only - the angle ϑ between the intermolecular axis R and the dipole moment vector μ.

Most authors choose for the attractive part of V terms corresponding to induction and dispersion forces:

$$V = - A(x) R^{-6} P_0 (\cos\vartheta) - B(x) R^{-6} P_2 (\cos\vartheta) , \quad (1)$$

where R is the distance between the centers of mass of the two molecules, and x is the vibrational coordinate describing the displacement from equilibrium positions of the vibrating

nuclei in the diatomic molecule.

More generally V may be written

$$V = \sum_k a_k (R,x) P_k (\cos \chi) . \tag{2}$$

The expectation values of the term $k = 0$ (the isotropic term) depend on the vibrational quantum number v only, while those of the terms $k \neq 0$ (the non-isotropic terms) depend, in addition to v, also on the rotational and spatial quantum numbers j and m.

In the static approach the difference in the perturbations of the upper and lower levels, $v'j^\circ m'$ and vjm, is calculated for a given position of the perturber and averaged over a static distribution of perturbers. Since in the line $v'j'vj$ the various $m \rightarrow m'$ transitions are not resolved, the perturbations of the frequency for a fixed position of the perturber must be averaged over all values of m and m'. To the first order in the interaction energy, where populations are equally distributed in the various substates of a level; and where the $m \rightarrow m'$ components are weighed with the unperturbed dipole transition moments, the frequency perturbation is independent of j. This is seen from the sumrules of dipole transition

moments and from a well known property of Legendre polynomials.[12] .

---

12. cf. Eq. (7) in I. For a detailed description of the averaging procedure, see ref. 6.

To account for the J-dependence, higher order effects have been considered (Buckingham[6]), such as Boltzmann distribution of populations in the m-states and second-order perturbations, without unqualified success. These treatments give poor results for low J, where the J-dependence is particularly marked. In these static theories it has been found necessary to resort to a modification of the model for close interaction distances, either by preferring one m state above others (Buckingham[6]) or by introducing an m-dependent collision diameter (Margenau[7]).

A consequence of Buckingham's static theory is that there should be an observable difference between the shifts of corresponding lines in emission and in absorption.[13] Recent experiments do not support this prediction.[14]

---

13. N.J. Bridge, and A.D. Buckingham, to be published.

14. J.H. Jaffe, K. Friedmann, M.A. Hirshfeld, and A. Ben-Reuven, to be published.

Static theories are valid when the only variation in time to be reckoned is the adiabatic limit is the continuous accumulation of phase shift due to the presence of a perturber. The shift is then given, as derived by Margenau,[7] by the average perturbation energy. The line shifts under discussion here were measured at low pressures (about one atmosphere), where all events during a collision occur in a very short time, as compared with the time between collisions. The change in a given line interval of the state of the molecular system then depends upon the number of collisions and consists of a succession of abrupt changes each due to one collision. For this case an impact approximation has been judged more appropriate.[15] The

___

15. The impact assumption was recently discussed by M. Baranger in _Atomic and Molecular Processes_ (Academic Press, New York and London, 1962), edited by D.R. Bates.

___

application, especially for strong collisions, yields completely different results, even in the adiabatic limit, from those obtained by the static approximation.

In an adiabatic collision a non-degenerate state
evolves (neglecting deformation effects) according to the same[16]

---

16. cf. H. Margenau, and M. Lewis, Rev. Mod. Phys., __ ___ (____).

$$\psi_i(t) = \psi_i(0) \exp\left[-\frac{i}{\hbar} \int E_i(t) \, dt \right]$$

where $E_i(t)$ is the instantaneous energy of the state i in
the configuration $R(t)$. Such a collision shifts the phase
of ψ_i by

$$\eta_i = \frac{1}{\hbar} \int_{coll.} V_i(t) \, dt \qquad (3)$$

where $V_i(t)$ is the perturbation of the energy of state i.
According to the impact approximation, the shift Δ^{if} of a
line $i \to f$ is then given (in wavenumbers) by[17]

---

17. H.M. Foley, Phys. Rev. __, ___ (1949).

$$\Delta^{if} = \frac{1}{2\pi c} \int d^3v \left[\eta_{if}(d^3r) \right] dv , \qquad (4)$$

where $\eta_{if} = \eta_f - \eta_i$ and dv is the rate of collisions

of type $d\sigma$. In the [unclear] denotes a certain choice of [unclear] relative velocity u and direction of [unclear] as the state of the perturbing atom. For [unclear] in their [unclear] state

$$dv = \frac{1}{2} \, n \, u \, f(u) \, b \, d b \, d u \, d\Omega,$$

where n is the density of perturbers, and $f(u)$ is the velocity distribution function.

A simple phase-shift method [unclear] be [unclear] to adiabatic collisions when one or both of the [unclear] are spatially degenerate. In the unperturbed [unclear] a definite m-state has a meaning only in relating it to a chosen quantization axis. When a perturbation is [unclear] on, there are non-vanishing transition probabilities between different m-states, which should also be related to the chosen quantization axis. Collisions are adiabatic in this case if the interaction energy causes large enough splitting of the degenerate states during the short time of the event. m will then remain a good quantum number in relation to that axis along which the interaction is diagonal — namely the internuclear axis $\underline{\rho}$. But then the effect of such a collision on the state function of the molecule expresses itself not only by a phase-shift,

in the sense of Eq. (3), but also by a rotational
transformation along with the rotation of $\vec{B}$ during the
collision.[18]

18. J. van Kranendonk, thesis, University of Amsterdam, 19...

Still another objection has been raised against the use of
the adiabatic assumption in a calculation of the shift by a
phase-shift method.[19] As collisions become stronger, their

19. L. Spitzer, Phys. Rev. 58, 348 (1940).

contribution to the shift increases with the phase shift η,
until $\sin\eta$ in Eq. (4) reaches its maximum value at $\eta = \pi/2$.
Still stronger collisions contribute less and, when η becomes
much larger than 2π, they add nothing more to the shift. In
fact, with straight-path collisions and an r^{-6} type interaction,
about three quarters of (4) come from collisions with $\eta < \pi/2$.
But an adiabatic assumption is valid only for strong enough
collisions, where the non-isotropic term in η is much larger
than unity. Therefore, unless by chance the isotropic and
non-isotropic parts of the phase-shift are both small, such only
adiabatic collisions will not make a major contribution to the
shift.

As has already been pointed out in I, on averaging η over the m, the contribution of the non-isotropic parts of the interaction vanishes. Some authors (Bagman, Herman), who use an average η, are therefore obliged to explain the j-dependence by assuming a j-dependence of the collision parameter, because collisions within the cut-off region are strong enough to cause appreciable transitions to different j-states. The weakness of this approach is that in order to obtain the right magnitude for the j-dependence it is found necessary to adopt values for the cut-off parameter that are much larger than the gas-kinetic diameters of the HCl-noble gas pairs. But there transition probabilities calculated with an interaction of type (1), are very small. Herman's treatment differs essentially from that of Anderson by introducing in the interaction energy, unlike most authors, an additional $P_1(\cos\chi)$ term which is more efficient than the P_2-term of (1) in causing perturbations. This term arises, according to Herman, from the spatial separation of the center of mass and center of charge interactions. In order to obtain good agreement with observation the center of interaction of HCl is assumed to be at about the mid-point between the chlorine and the hydrogen nuclei. This choice is open to criticism because the main contributions to the polarizability are from the outer shells

electrons of the chlorine atom and the two valence electrons
which are also more closely bound to the chlorine atom.

A treatment having features in common with the one set
out below has been presented independently by Schuller and
Oksengorn,[10] who pointed out that it is the expression (4)
for the line shift (involving $\sin\eta$, and not η itself) that
should be averaged over all m-states. However, Schuller and
Oksengorn based their calculation of the phase-shift on the
assumption of adiabatic collisions, and did not take into
account the rotation of the quantization axis during the
collision process.

A CORRECT PHASE-SHIFT APPROXIMATION

The shift may indeed be calculated from Eq. (4) with $\sin\eta$
(and not η) averaged over m-states, provided that a phase-shift
approximation holds with respect to a reference system fixed
in space for a given collision. Generally a collision will cause
transitions between the various m-states, whose probability
depend on the choice of the coordinate system. However there
exists a choice of axis (the space line of the collision) with
respect to which these effect is relatively small and, under
some restricting conditions, a phase-shift approximation can be

used with the phase shifts η referred to that particular fixed coordinate system. Here again, as in the adiabatic approach, the interaction of different j-states is neglected.

According to Anderson,[20] the exact expression in the

20. P.W. Anderson, Phys. Rev. 76, 647 (1949).

impact limit for the width and shift of an isolated line $j \rightarrow j'$, with degenerate levels, is

$$\tfrac{1}{2}\Gamma - i\Delta - \frac{1}{2\pi c}\int \text{...} \, S(d\sigma)$$

where, in Anderson's notation,

$$S(d\sigma) = 1 - \frac{\text{Trace}\left\{\mu^{jj'} \, T^{\dagger j'j'}(d\sigma) \, \mu^{j'j} \, T^{jj}(d\sigma)\right\}}{\text{Trace}\left\{\mu^{jj'} \, \mu^{j'j}\right\}} \qquad (5)$$

Here $T(d\sigma)$ is the scattering operator for the internal states of the molecule corresponding to collision of type $d\sigma$; μ is the dipole moment operator along the polarization direction of the absorbed photon. The trace is taken over the sub-spaces of the initial and final degenerate levels.

Among other parameters which determine $d\sigma$ is the orientation of the collision with respect to the polarization axis, taken as the z-axis. But, noting that (5) is invariant under rotation of the coordinate system, the roles of the collision orientation and the polarization axis may be interchanged. Choosing some direction defined by the collision as a z-axis, the averaging can be made over all possible directions of the polarization axis, by summing (5) over the three components of μ in the system defined by the collision. The relation of this system to the orientation of the collision is immaterial in the calculation of $S(d\sigma)$ as a whole. Yet individual matrix elements of T in (5) may depend on it, due to the spatial degeneracy. By a particular choice of z-axis, namely the apse line (the intermolecular axis at the moment of closest approach), the non-diagonal matrix elements of T connecting different m-states can be made small, compared with the diagonal elements. Then, if inelastic transitions are negligible,

$$\langle vjm \,|\, T \,|\, vjm'' \rangle \approx \exp\left[-i\eta_{vjm}\right]\delta_{mm''} \quad ,$$

where

$$\eta_{vjm} = -\frac{1}{\hbar} \int_{coll} \langle vjm | V(t) | vjm \rangle \, dt \quad , \qquad (6)$$

with V represented in the fixed system. Expression (5) then reduces to the phase-shift expression

$$S(d\sigma) = 1 - \sum_{mm'} z_{mm'}^{jj'} \exp\left[i(\eta_{v'j'm'} - \eta_{vjm})\right] \, , \quad (7)$$

where $z_{mm'}^{jj'}$ are the (normalized) dipole transition moments. The resulting line shift is

$$\Delta^{jj'} = \frac{1}{2\pi c} \sum_{mm'} z_{mm'}^{jj'} \int d\nu \, \sin\left(\eta_{v'j'm'} - \eta_{vjm}\right) \, . \quad (8)$$

Anderson has given an iteration process for the calculation of T in power series of the operator P, whose matrix elements are given by

$$\langle a | P | b \rangle = \frac{1}{\hbar} \int_{coll} e^{i\omega_{ab}t} \langle a | V(t) | b \rangle \, dt \quad ,$$

thus obtaining[21]

---

21. P.W. Anderson, thesis, Harvard (1949). Equation (9)

    is obtained by neglecting the non-commuting of $V(t_1)$

    and $V(t_2)$ at two different moments t_1 and t_2.

    The non-commuting terms are shown to lead to the

    introduction of higher-order perturbations.

$$T = 1 - iP - \frac{1}{2} P^2 + \ldots \tag{9}$$

Tsao and Curnutte[22] have given a calculation of $\langle a \mid P \mid b \rangle$

---

22. C.J. Tsao, and B. Curnutte, J. Quant. Spectrosc. Radiat.

    Transfer, 2, 41 (1962).

---

for the interaction term with $P_2(\cos\chi)$. It was shown that
for a straight path collision with impact parameter b and
relative velocity u (fig. 1a), matrix elements of P between
two different energy states j and j" include the factor
$\exp(-\omega_{jj''}b/u)$ which becomes exceedingly small when $\omega_{jj''}b/u \gg 1$.
In the case of collisions between HCl and the heavier noble gas
atoms, with impact parameter larger than the gas-kinetic collision
diameter, and average velocities corresponding to temperatures as

high as $1000^{\circ}C$, this inequality generally holds and matrix elements of P between two j levels are negligible.

To calculate the matrix elements of P in the sub-space of the level j, with a given fixed quantization axis, it is necessary to rewrite $P_2(\cos\chi)$ in terms of the polar angles (θ, ϕ) of $\underset{\sim}{\mu}$ and (θ_R, ϕ_R) of $\underset{\sim}{R}$ in the given reference system. This is done by the addition theorem for Legendre polynomials,[23]

---

23. cf. E.U. Condon, and G.H. Shortley, <u>The Theory of Atomic Spectra</u> (Cambridge University Press, New York, 1935).

$$P_k(\cos\chi) = \frac{4\pi}{2k+1} \sum_{\lambda=-k}^{k} Y^*_{k,\lambda}(\theta, \phi) Y_{k,\lambda}(\theta_R, \phi_R) , \quad (10)$$

where, unlike the operators $Y_{m,\lambda}(\theta, \phi)$, the expressions $Y_{k,\lambda}(\theta_R, \phi_R)$ are functions of the classical path parameters $\theta_R(t)$ and $\phi_R(t)$.

The matrix elements $\langle jm | Y^*_{k,\lambda}(\theta, \phi) | jm'' \rangle$ vanish unless $m'' = m + \lambda$. Therefore, in the non-diagonal matrix elements $\langle jm | P | jm'' \rangle$, only those terms appearing in (10) need be retained for which $\lambda \neq 0$. Now, if $\lambda \neq 0$, the integrals $\int a_k(R) Y_{k,\lambda}(\theta_R, \phi_R) dt$ which appear in $\langle jm | P | jm'' \rangle$ are minimized by taking the z-axis in the direction where $a_k(R)$ has a sharp maximum. This is due to the fact that all spherical

harmonics with $\lambda \neq 0$ vanish along the z-axis $(\theta_R = 0)$.
In this work, where the interaction (1) is assumed, the
integrals

$$\int R^{-6} Y_{2,\lambda}(\theta_R, \phi_R)dt = g_\lambda$$

should be considered. Performing the integration along a
straight path, with the z-axis perpendicular to, and the x-axis
along the path, one obtains $g_{\pm 1} = 0$, while $g_{\pm 2} = g_0/\sqrt{54}$.

In the diagonal matrix elements of P, which give the phase
shift, the following integrals must be considered

$$\int \hbar^{-1}R^{-6}\langle jm \,|\, P_k(\cos\mathcal{X})\,|\, jm\rangle \; dt = \langle jm \,|\, P_k(\cos\theta)\,|\, jm\rangle \int \hbar^{-1}R^{-6} P_k(\cos\theta_R) \; dt, \quad (11)$$

where $k = 0,2$. For straight path collisions, in which $R^2 = u^2 t^2 + b^2$,

$$\int_{-\infty}^{\infty} \hbar^{-1}R^{-6}dt = \frac{3\pi}{8\hbar u b^5} = G, \qquad (12)$$

and

$$\int_{-\infty}^{\infty} \hbar^{-1}R^{-6}P_2(\cos\theta_R)dt = \frac{3}{4}G. \qquad (13)$$

The phase shift

$$\eta_{mm'} = \eta_{v'j'm'} - \eta_{vjm}$$

for the $m \to m'$ component of the line now becomes, using (6), (1), (11), (12) and (13),

$$\eta_{mm'} = -\left[(A_{v'} - A_{v}) + \tfrac{3}{4}(B_{v'}\langle j',m'\rangle - B_{v}\langle j,m\rangle)\right] G, \quad (14)$$

where

$$\langle j,m\rangle = \langle jm \mid P_2(\cos\theta)\mid jm\rangle = \frac{j(j+1) - 3m^2}{(2j-1)(2j+3)},$$

and where[24] $A_v = \langle v \mid A(x)\mid v\rangle$, $B_v = \langle v \mid B(x)\mid v\rangle$.

---

24. For the HCl molecule, in the range of j to which the present theory was applied ($j \leqslant 7$), the effect of centrifugal stretching, which introduces a j-dependence into the vibrational expectation values, is very small and was therefore neglected. At higher j it may cause a small measureable effect, shifting lines in the R-branch more to lower frequencies than corresponding lines in the P-branch (cf. the C-term in Eq. (28) of ref. 6).

The non-diagonal matrix elements $\langle jm \mid P \mid jm''\rangle$ are small compared with $\eta_{mm'}$, unless the isotropic and non-isotropic parts of $\eta_{mm'}$ happen almost to cancel each other. But then the contribution of such an $m \to m'$ component to the total shift is in any case small, and the error introduced in the calculation of the shift by neglecting the non-diagonal elements is small.

An estimate of the error introduced by neglecting the non-diagonal matrix elements $\langle jm \mid P \mid jm'' \rangle$ may be reached by comparing an expansion of (7) in power series of P to the iteration process of Anderson, where the $\langle jm \mid P \mid jm'' \rangle$ are included in a similar expansion of (5)[20]:

$$S(d\sigma) = S_0 + iS_1 + S_2 + \ldots$$

In both approaches S_0 vanishes, and $-S_1$ is equal to the average over m-states of the phase-shift. In this last term, which gives the first-order contribution to the shift, only the isotropic part $-(A_{v'} - A_v)G$ remains, and therefore S_1 fails to account for the j-dependence of the shift. The next term is

$$S_2 = \frac{1}{2} G^2 \left\{ (A_{v'} - A_v)^2 + \xi \sum_{mm'} z_{mm'}^{jj'} (B_{v'} \langle j',m' \rangle - B_v \langle j,m \rangle)^2 \right\} .$$

In Anderson's exact expansion the numerical coefficient ξ is equal to $7/12$, whereas in the present phase-shift approximation $\xi = 9/16$. The difference between the two is a factor $27/28$

only.[25] In S_3, which gives an important contribution to

---

25. In the adiabatic approach of Schuller and Oksengorn
    (ref. 10), $\xi = 1$ instead of 7/12.

---

the shift, the difference is not much larger.[26]

---

26. The coefficients B_v and $B_{v'}$ are usually much larger than
    $(A_{v'} - A_v)$, and therefore even with collisions where S_1 is
    still small, the individual phase-shifts $\eta_{mm'}$ may be quite
    large and S_3 may be very important.

A collision in which a j-transition occurs does not
contribute to the line shift and it therefore seems reasonable
as suggested by Englman to exclude those collisions whose
parameter lies within the cross-section for j-transitions.[9]
Since this cross-section is j-dependent (because the spacing
between adjacent j levels increases with j) such a cut-off
treatment would predict an additional j-dependence of the line
shift that may bring about an improvement over the results of
the phase-shift method.

-21-

Unfortunately, very little is known about the cross-section for j-transitions in HCl - noble gas collisions, though it is generally accepted that it is of the order of magnitude of the gas-kinetic cross-section.[27] However, as is seen from

27. cf. H.S.W. Massey, and E.H.S. Burhop, Electronic and Ionic Impact Phenomena (Oxford, at the Clarendon Press, 1952).

the results of the present work, an approximation wherein a cut-off at b = d is applied for all lines, yields by and large the right magnitude and form of the j-dependence, using the interaction energy (1), with the various force constants calculated in the normal manner for induction and dispersion forces. Possible refinements, involving collisions with b<d and accounting for j-transitions, are discussed briefly in a concluding paragraph of this paper.

CALCULATION OF THE SHIFT

The cross-section for the shift is expressed for convenience in terms of the billiard-ball cross-section πd^2, and as a function of the parameters $K_{mm'}$, defined as the phase-shift (14)

for b = d:

$$K_{mm'} = \eta_{mm'}(d) \quad .$$

With the collision rate $dv = 2\pi\, n\, u\, b\, db$, the shift given by (8) can be written[28]

---

28. An averaging should be made over a distribution of the
    relative velocities u. This problem has been treated by
    Schuller and Oksengorn (ref. 10). Nevertheless it is
    usually sufficient to take an average value of u.

$$\Delta^{jj'} = \frac{nu}{2\pi c}\; \pi d^2 \sum_{mm'} z_{mm'}^{jj'}\; \Phi(K_{mm'}),$$

where

$$\Phi(K_{mm'}) = \int 2(b/d)\sin(\eta_{mm'})\,d(b/d).$$

In the approximation where collisions with $b < d$ are excluded (the "cut-off" approximation),

$$\Phi(K) = \Phi_{c.o.}(K) = \frac{2}{5}K^{2/5}\int_0^K \eta^{-7/5}\sin\eta\,d\eta.$$

To give an idea of the contribution to the shift from collisions

with $b < d$, leaving aside j-transitions, $\Phi_{c.o.}(K)$ is compared in Fig. 2 with two other approximations, where phase-shifts from close collisions are included. One of them (the "straight-path" approximation) is the less realistic, though more commonly used, where the size of the molecules is neglected and all collisions ($o < b < \infty$) are considered with straight paths. Note that the corresponding expression

$$\Phi(K) = \Phi_{s.p.}(K) = \frac{2}{5} K^{2/5} \int_0^K \eta^{-7/5} \sin\eta \, d\eta = 0.8753 \, K^{2/5},$$

when multiplied by d^2, is independent of d. The other, more realistic approach is based on the suggestion of Schuller and Vodar[29] to use the model of rigid spheres,

---

29. F. Schuller, and B. Vodar, Compt. rend. 251, 1877 (1960).

---

with broken paths for collisions with $b < d$ (Fig. 1b). Taken along a broken path, the integral (13) is no longer three-quarters of the integral (12). The ratio of the two integrals changes with b, from 3/4 for $b = d$, to 1 for $b = 0$ (the limit where adiabatic and phase-shift treatments coincide). The plot of $\Phi_{b.b}(K)$ (the "billiard-ball" approximation) given in fig. (2)

was calculated by assuming the constant ratio 3/4 all over the range of variation of b, thus introducing a small error, which vanishes in the limiting case where only the isotropic part of the interaction contributes to the shift.

As the angular momentum j increases, the sum $\sum_{mm'} z_{mm'}^{jj'} \Phi(K_{mm'})$ converges into the term $\Phi(K_{vv'})$, where $K_{vv'}$ is the contribution to $K_{mm'}$ from the isotropic part of the interaction. Therefore, the shift should tend with increasing j-number to a value which depends on vibrational quantum numbers only. It is interesting to notice that in the interval $0 < K \lesssim 3$, both $\Phi_{c.o.}$ and $\Phi_{b.b.}$ are nearly linear in K, while $\Phi_{s.p.}$ is proportional to $K^{2/5}$. This distinction is important for the interpretation of the ratio of the shifts of corresponding lines in the fundamental and overtone vibrational bands.

The parameters A and B in the interaction energy (1) were calculated in a manner similar to that of I, with the additional refinements that the vibrational dependence of the anisotropy of the polarizability was considered, and the average electronic energy W, which appears in the dispersion interaction, was determined in a different manner.

We write

$$A = \alpha_b \mu_a^2(x) + \tfrac{3}{4}\alpha_a(x)\alpha_b W$$

and

$$B = \alpha_b \mu_a^2(x) + \tfrac{3}{4}\gamma(x)\alpha_a(x)\alpha_b W$$

where α_a and α_b are the polarizabilities of the polar molecule and the noble gas atom respectively; $\gamma = (\alpha_\| - \alpha_\perp)/(2\alpha_\perp + \alpha_\|)$ is the anisotropy in α_a due to the difference between the polarizability $\alpha_\|$ along and $\alpha_\perp$ perpendicular to the molecule's symmetry axis. W was determined by comparing the ground-state value of A with an empirical value of the force constant (the $4\epsilon\sigma^6$ term of a Lennard-Jones 6-12 potential energy function[30]

30. cf. J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, _Molecular_

Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1954).

with ϵ and σ for the mixture of two gases calculated by the mixing rules $\epsilon = (\epsilon_a \cdot \epsilon_b)^{1/2}$, $\sigma = \tfrac{1}{2}(\sigma_a + \sigma_b)$.

The variation of A and B with the vibrational quantum number was calculated by expanding $A(x)$ and $B(x)$ to the first power of x :

$$A(x) = A_0 + \left[\partial A(x)/\partial x\right]_{x=x_0} (x-x_0) + \dots ,$$

with $x_0 = \langle o|x|o\rangle$. Now

$$\partial A/\partial x = 2\alpha_b \mu_a \partial \mu_a/\partial x + \tfrac{3}{4}\alpha_b W \partial\alpha_a/\partial x ,$$

and

$$\partial B/\partial x = 2\alpha_b \mu_a \partial \mu_a/\partial x + \tfrac{3}{4}\alpha_b W \partial(\gamma\alpha_a)/\partial x.$$

If however $\partial\alpha_\perp/\partial x \ll \partial\alpha_\parallel/\partial x$, as is true for HCl (both from empirical evidence[31] and from theoretical

---

31. E.J. Stansbury, M.F. Crawford, and H.L. Welsh, Can. J. Phys. 31, 954 (1953).

---

considerations[32]), then $\partial(\gamma\alpha_a)/\partial x \approx \partial\alpha_a/\partial x$,

---

32. F. Schuller, L. Galatry, and B. Vodar, Compt. rend., 248, 2194 (1959).

---

and therefore $\partial B/\partial x \approx \partial A/\partial x$. In this case $K_{mm'}$ may

be written

$$K_{mm'} = K_{vv'} \left[1 + \frac{3}{4} \frac{B_v}{\Delta A} (\langle j', m' \rangle - \langle j, m \rangle) + \frac{3}{4} \langle j', m' \rangle \right] ,$$

with

$$K_{vv'} = - \frac{3\pi \Delta A}{8 \hbar u d^5} ,$$

where $\Delta A = A_{v'} - A_v$. Values of $K_{vv'}$ and $B_v / \Delta A$, for HCl collisions with the noble gases argon, krypton and xenon at room temperature, have been calculated using the values of $\alpha_a, \partial \alpha_a / \partial x, \gamma, \alpha_b, \mu_a, \partial \mu_a / \partial x, \langle v | x | v \rangle, \sigma_a, \sigma_b, \epsilon_a,$ and $\epsilon_b,$ which are listed in I. These are gathered in Table I, together with d, u, and W. The values of B_v were obtained by considering only the known anisotropy of the polarizability. A similar anisotropy in W may add to the magnitude of the anisotropic interaction. Therefore values of $B_v / \Delta A$ higher by 50% than those given in Table I were also used in the calculations.

DISCUSSION OF RESULTS

The line-shifts induced by argon and krypton in the 1-0 and 2-0 bands of HCl, calculated with the "cut-off" approximation,

are shown in Figs.3 and 4, together with the experimental
points. In each case two curves are given, one with values
of $K_{vv'}$ and $B_v/\Delta A$ calculated from the molecular constants
alone (see Table I) and a second with a value of $B_v/\Delta A$
set 50% higher.

In Fig. 5 the experimental shifts in the 1-0 band of
HCl pressurized by krypton are compared with calculated
values using the broken-path "billiard-ball" approximation,
in addition to those obtained by the "cut-off" approximation.
At higher j-values the experimental points lie between the
two curves. This suggests that with increasing j, as
j-transitions become less probable, more and more contribution
to the shift comes from the region of close collisions ($b < d$).
A better agreement with experiment would thus be obtained by
using a j-dependent cut-off (falling in the region $b < d$).

Very recent work[33] has revealed that shifts of HCl 2-0 band

33. D.H. Rank (private communication; Revs. Mod. Phys.
    34, 577 (1962)) has given observed values of shifts of HCl
    lines due to argon and xenon up to j = 23; due to krypton
    up to j = 15.

lines due to argon do not tend to a constant limit for high j
but begin to decrease at about j = 8.

There is then a systematic trend: shifts due to helium
are all towards higher frequencies; those due to neon pass a
maximum red shift at about j = 3; with argon the maximum is
at about j = 8; with krypton the shift is still fairly constant
at about j = 15; and with xenon the shifts are still increasing
with j at j = 23.

These manifestations may be explained by taking into
consideration short range forces. As explained above, with
increasing j, closer and closer collisions contribute to the
observed shifts and therefore short range forces become more
and more important. Moreover, weakly interacting lighter noble
gases are less effective in causing j-transitions than the
strongly interacting heavier ones. Consequently the values of
j at which the region of close collisions assumes importance
increase progressively from helium to xenon. In this region
it is necessary to consider in addition to repulsive forces
also short range attractive forces (such as the R^{-8} dispersion
interaction[30], which increases with the square of the
polarizability of HCl), whose relative importance increases from

the lighter noble gases to the heavier ones. These attractive forces lead to an increase in the red shifts with xenon, whereas with neon and argon the repulsive forces predominate in short range collisions and the trend is opposite.

In the light of the above discussion some features of the temperature dependence of the shifts may be understood qualitatively as follows. As the temperature increases, the mutual penetration of the colliding molecules increases and therefore the importance of short-range interactions becomes more marked. The shifts may be expected to increase with temperature with the heavier noble gases (xenon) and decrease with the lighter ones (argon, at higher j). These opposite tendencies were in fact observed in measurements of the temperature dependence of shifts induced by xenon and by argon.[4,33]

The present theory fails to account for the shifts of the two lines in the center of the band - R(0) and P(1). This may be due to the inadequacy of first-order perturbation treatment, as well as to the larger probability of j-transitions outside the region $b < d$ (both because of the small separation of the rotational energy levels $j = 0$ and $j = 1$).

It is hoped that a future investigation, where j-transitions and short-range forces are duly considered, will extend the validity of the present treatment to account for all observed features (including effects of temperature) of the HCl shifts induced by the noble gases.
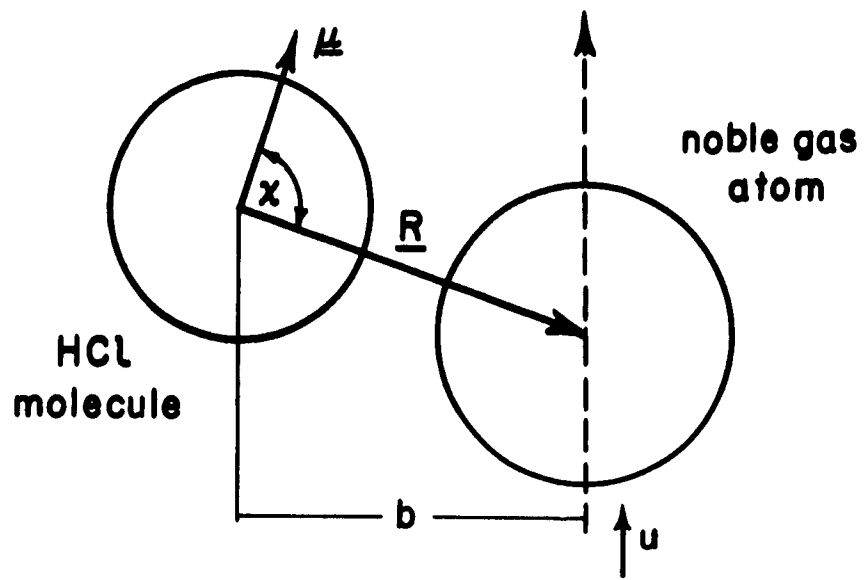
ACKNOWLEDGEMENTS

TABLE I

Values of the billiard-ball radius d, relative velocity u, average electronic energy W, the parameters $K_{vv'}$ and $B_v/\Delta A$ for interactions of HCl with argon, krypton and xenon.
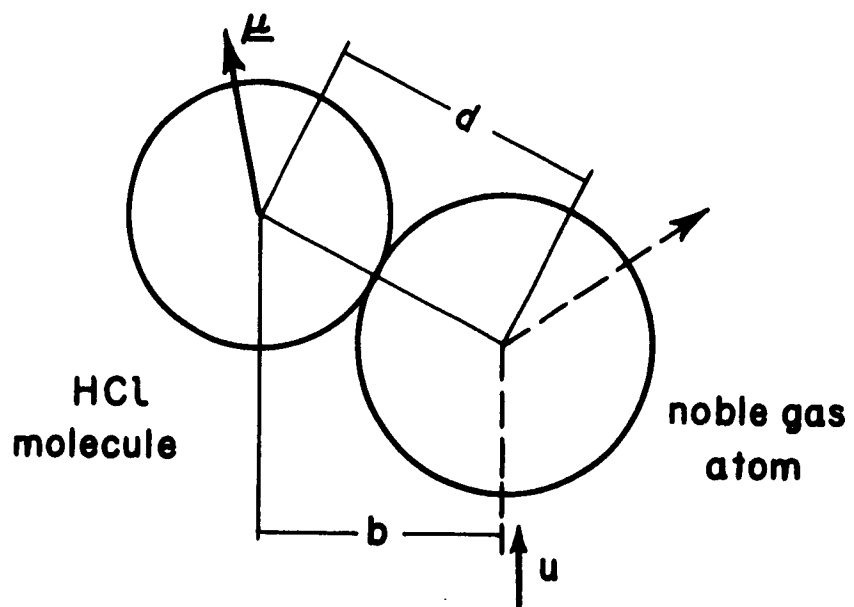
		Ar	Kr	Xe
d (in 10^{-8}cm)		3.21	3.31	3.53
u (in 10^4cm sec^{-1})		5.75	4.98	4.69
W (in 10^{-12}erg)		51.3	47.0	47.5
$K_{vv'}$	1-0 band	-1.05	-1.45	-1.82
	2-0 band	-2.45	-3.40	-4.26
$B_v/\Delta A$	1-0 band	9.6	9.6	9.6
	2-0 band	4.1	4.1	4.1

CAPTIONS OF FIGURES
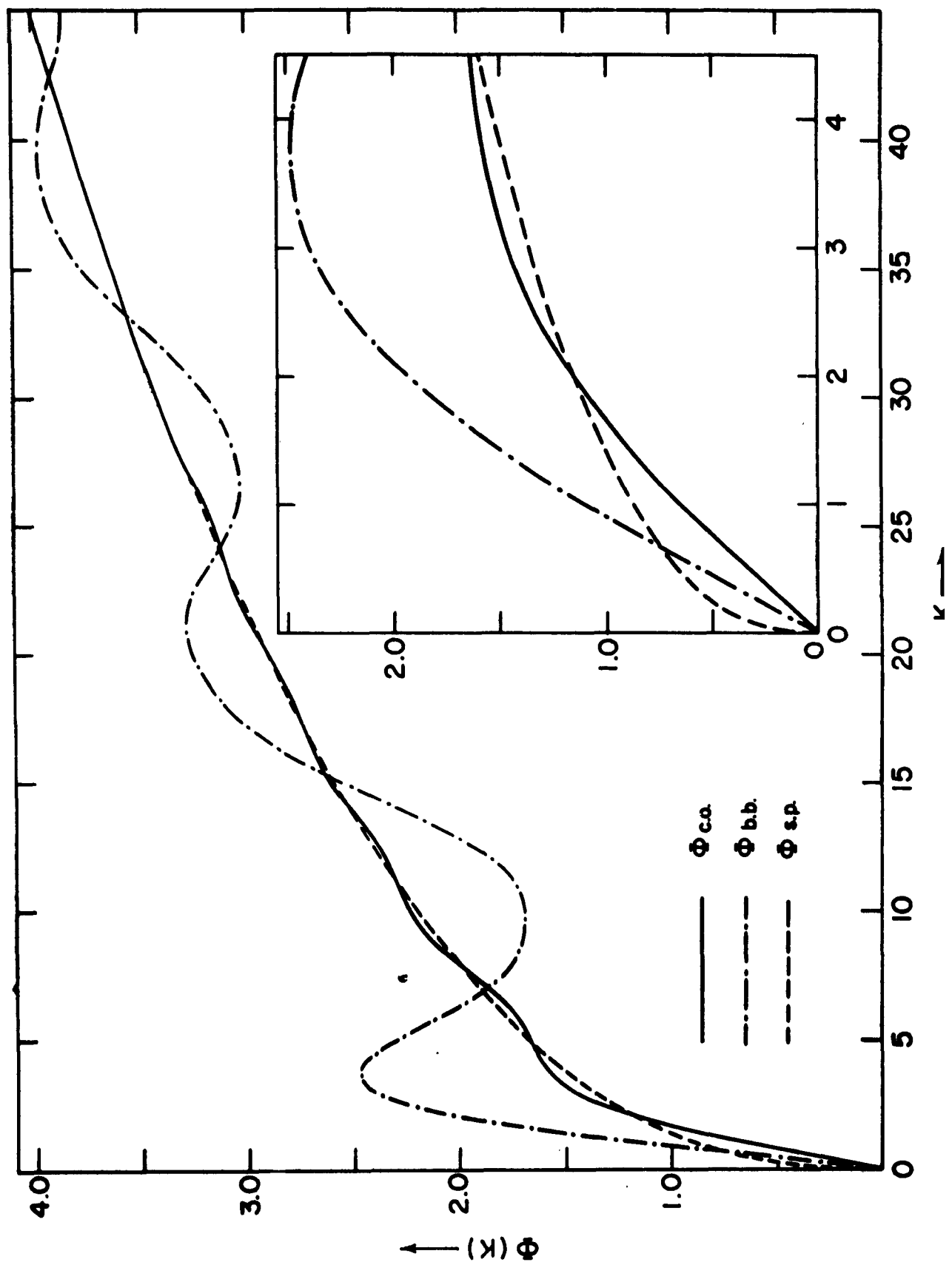
Fig. 1   The "billiard-ball" collision model with (a) impact
          parameter b larger than billiard-ball radius d,
          and (b) b smaller than d.

Fig. 2   The shift factors $\Phi(K)$ for the "cut-off", "billiard-
          ball", and "straight-path" approximations.

Fig. 3   Argon-induced shifts of HCl lines calculated with the
          "cut-off" approximation, with values of $K_{vv'}$ and
          $B_v/\Delta A$ given in Table I, and with values of $B_v/\Delta A$
          50% higher.

Fig. 4   Krypton-induced shifts of HCl lines calculated with the
          "cut-off" approximation, with values of $K_{vv'}$ and
          $B_v/\Delta A$ given in Table I, and with values of $B_v/\Delta A$
          50% higher.

Fig. 5   Shifts due to krypton in the 1-0 band of HCl calculated
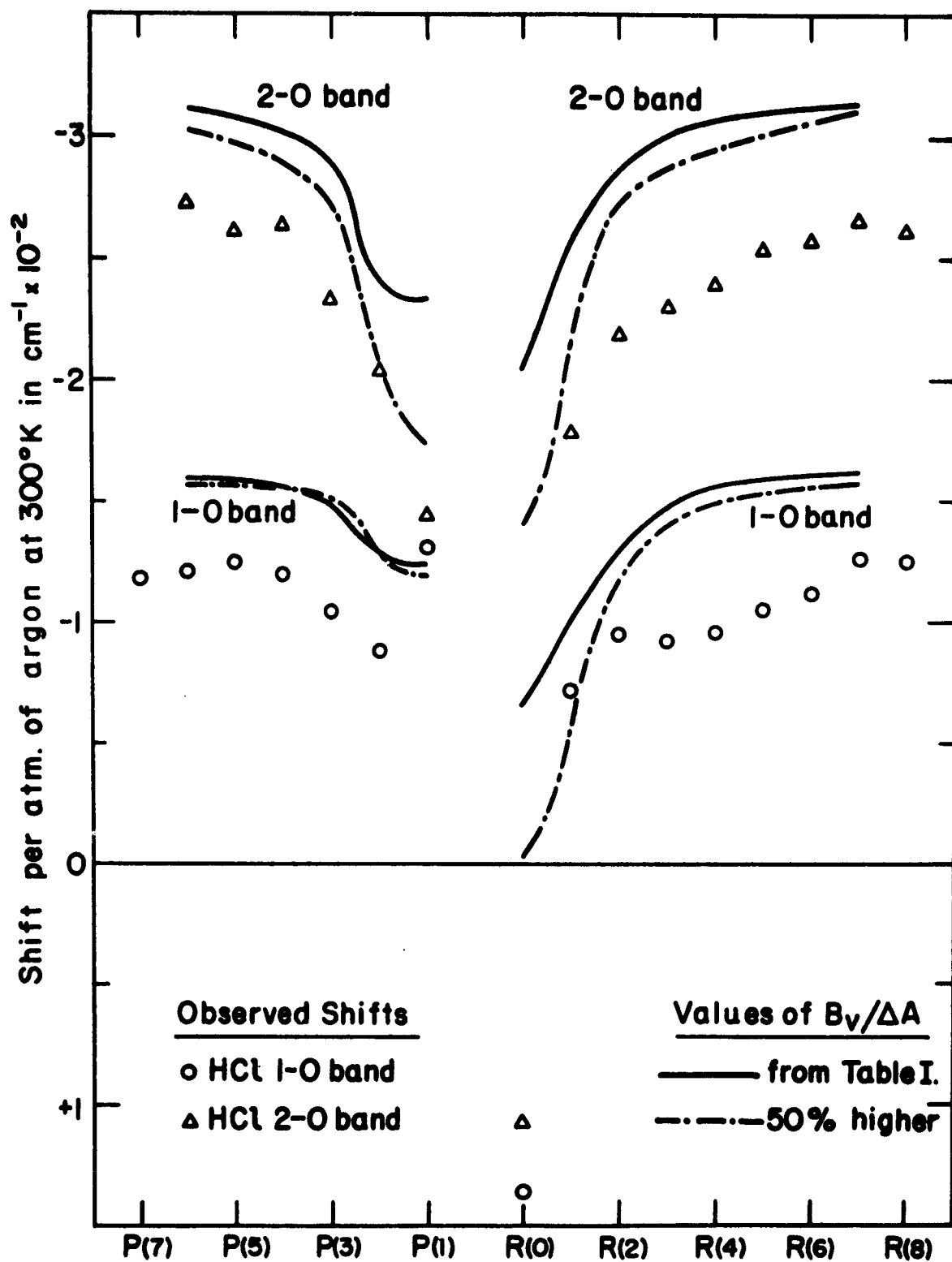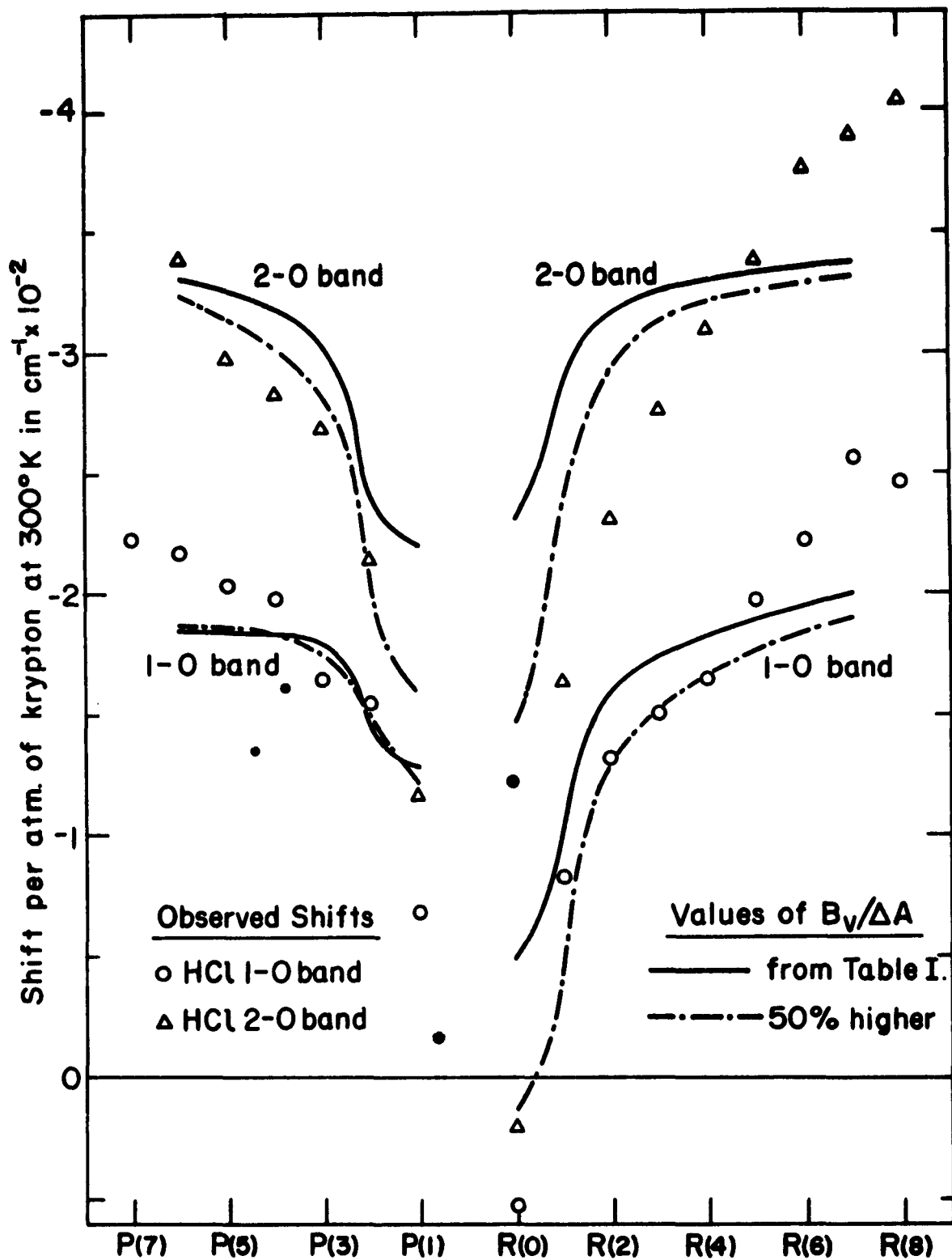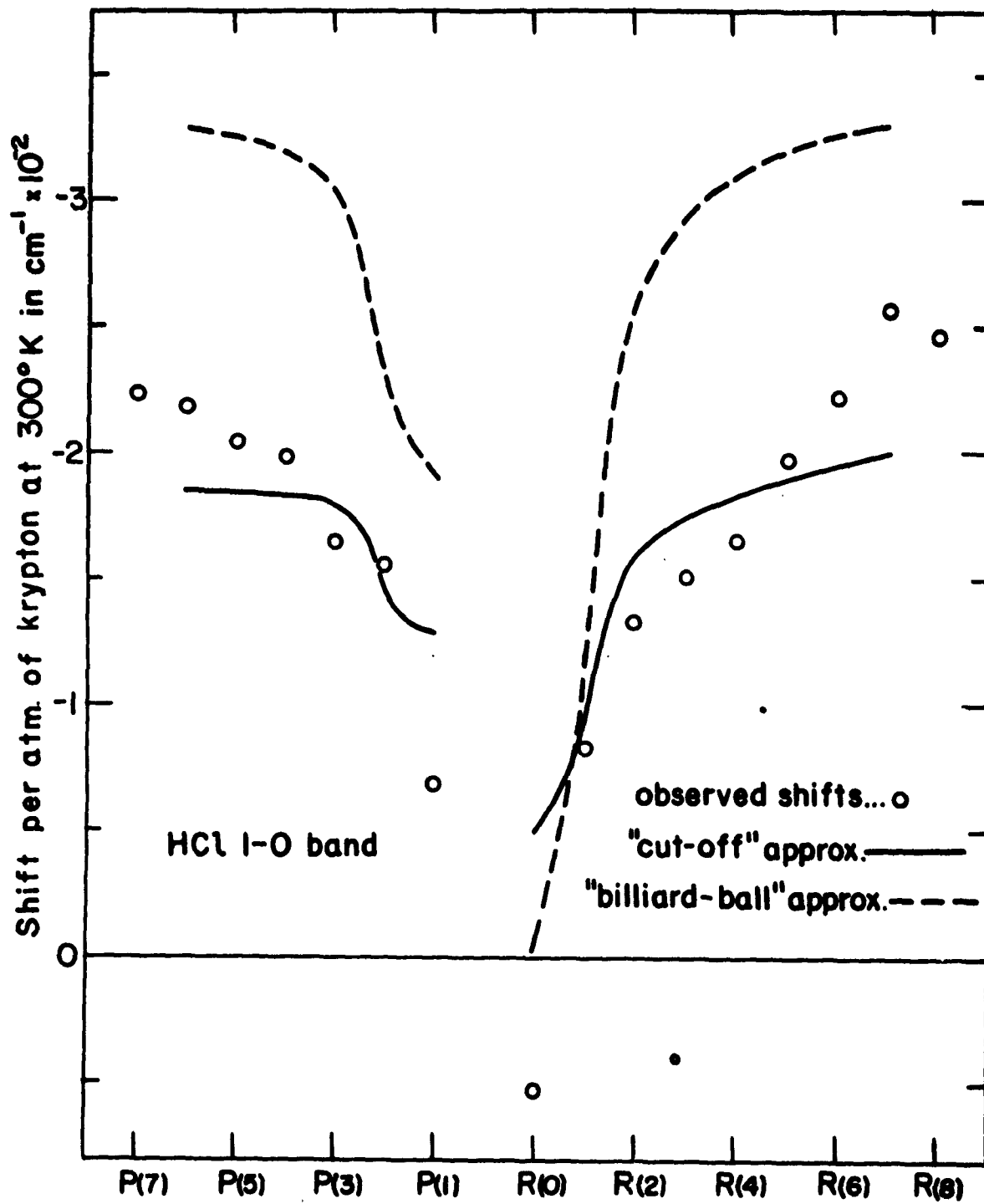   with the "cut-off" and "billiard-ball" approximations.

(a)

(b)

HCl 1-O band

observed shifts...○
"cut-off" approx. ——
"billiard-ball" approx. ----

ASTIA NR.
Contract Nr. AF 61(052)-388
United States Air Force, Air Research and
Development Command, European Office,
Brussels, Belgium.

ANNUAL SUMMARY REPORT No. 2

February 1963

Weizmann Institute of Science,
Rehovoth.

ABSTRACT: (See reverse side)

ASTIA NR.
Contract Nr. AF 61(052)-388
United States Air Force, Air Research and
Development Command, European Office,
Brussels, Belgium.

ANNUAL SUMMARY REPORT No. 2

February 1963

Weizmann Institute of Science,
Rehovoth.

ABSTRACT: (See reverse side)

ASTIA NR.
Contract Nr. AF 61(052)-388
United States Air Force, Air Research and
Development Command, European Office,
Brussels, Belgium.

ANNUAL SUMMARY REPORT No. 2

February 1963

Weizmann Institute of Science,
Rehovoth.

ABSTRACT: (See reverse side)

ASTIA NR.
Contract Nr. AF 61(052)-388
United States Air Force, Air Research and
Development Command, European Office,
Brussels, Belgium.

ANNUAL SUMMARY REPORT No. 2

February 1963

Weizmann Institute of Science,
Rehovoth.

ABSTRACT: (See reverse side)

ABSTRACT: This report contains a summary of recent efforts to form a theory of pressure induced shifts of lines in molecular spectra due to noble gases. A treatment is presented that accounts to a large extent for the j-dependence of pressure induced shifts due to noble gases of lines in HCl bands. After a brief critical review of the theoretical work done on this subject to date, an improved phase-shift approximation for the intermolecular collision process is worked out with a coordinate system fixed in space during the collision. The main features of the observed phenomena are accounted for using only parameters calculated directly from known molecular properties. A discussion of the limitations of this theory is given. It appears that in order to achieve further improvement, the finite probability of j-transitions and the influence of short-range forces should be taken into account.

ABSTRACT: This report contains a summary of recent efforts to form a theory of pressure induced shifts of lines in molecular spectra due to noble gases. A treatment is presented that accounts to a large extent for the j-dependence of pressure induced shifts due to noble gases of lines in HCl bands. After a brief critical review of the theoretical work done on this subject to date, an improved phase-shift approximation for the intermolecular collision process is worked out with a coordinate system fixed in space during the collision. The main features of the observed phenomena are accounted for using only parameters calculated directly from known molecular properties. A discussion of the limitations of this theory is given. It appears that in order to achieve further improvement, the finite probability of j-transitions and the influence of short-range forces should be taken into account.

ABSTRACT: This report contains a summary of recent efforts to form a theory of pressure induced shifts of lines in molecular spectra due to noble gases. A treatment is presented that accounts to a large extent for the j-dependence of pressure induced shifts due to noble gases of lines in HCl bands. After a brief critical review of the theoretical work done on this subject to date, an improved phase-shift approximation for the intermolecular collision process is worked out with a coordinate system fixed in space during the collision. The main features of the observed phenomena are accounted for using only parameters calculated directly from known molecular properties. A discussion of the limitations of this theory is given. It appears that in order to achieve further improvement, the finite probability of j-transitions and the influence of short-range forces should be taken into account.

ABSTRACT: This report contains a summary of recent efforts to form a theory of pressure induced shifts of lines in molecular spectra due to noble gases. A treatment is presented that accounts to a large extent for the j-dependence of pressure induced shifts due to noble gases of lines in HCl bands. After a brief critical review of the theoretical work done on this subject to date, an improved phase-shift approximation for the intermolecular collision process is worked out with a coordinate system fixed in space during the collision. The main features of the observed phenomena are accounted for using only parameters calculated directly from known molecular properties. A discussion of the limitations of this theory is given. It appears that in order to achieve further improvement, the finite probability of j-transitions and the influence of short-range forces should be taken into account.