Semi-experimental Determination of a Repulsive Potential Curve for Hydrogen Iodide

BY J. F. OGILVIE

Department of Chemistry, Memorial University of Newfoundland,
St. John's, Nfld., Canada

Received 7*th December*, 1970

New measurements of the extinction coefficients of hydrogen and deuterium iodide vapours have been made in the spectral region 32 000 to 52 000 cm^{-1}. Combining these data with anharmonic vibrational probability functions based on spectroscopic parameters and containing a dependence on rotational quantum number has permitted calculation of potential curves for the repulsive upper state of the continuum of the electronic transition. Separate, apparently distinct potential curves for HI and DI were obtained, but accumulated experimental inaccuracies are probably responsible for the discrepancies. The equation describing the repulsive potential curve of HI is

$$V(x) = 25\,707+(20\,982\pm84)\exp[(-5.350\pm0.049)x]$$

From the continuous electronic absorption spectrum of hydrogen iodide vapour Goodeve and Taylor [1] tried to construct a portion of the potential curve of the upper state, which was deduced to be repulsive. About the same time, by measurements of the deuterium isotope effect on the small wavenumber wings of the continuum, Bates, Halford and Anderson [2] demonstrated that the absorption coefficients of both hydrogen bromide and hydrogen iodide substantially exceeded those of the corresponding deuterium halides at particular wavenumbers in this spectral region. In all these cases, the maxima of the continua were not definitely observed.

In recent years, these tasks have become much easier both experimentally and theoretically. Publication of spectroscopic parameters from extensive vibration-rotational absorption spectra has allowed a moderately accurate knowledge of the potential curve of the ground electronic state, at least near the minimum of this curve, and accurate anharmonic-oscillator vibrational wavefunctions (including a dependence on rotational quantum number J) have recently become available in a readily usable form.[3] Both of these factors have contributed to the present interpretation of the continuous electronic absorption spectra of hydrogen and deuterium iodide vapours. The result of the study is a fairly accurate determination of a potential energy function for a repulsive excited state of a diatomic molecule. Although very few determinations, either experimental or *ab initio* theoretical, of repulsive potentials have been made,[4] hydrogen iodide is extremely favourable for this purpose because its electronic absorption continuum lies in a readily accessible region.

EXPERIMENTAL

Hydrogen and deuterium iodides were separately prepared by reaction of phosphoric acid with potassium iodide in vacuo or by reaction of H_2O or D_2O under nitrogen with a mixture of red phosphorus and iodine. They were first dried by passage over phosphorus pentoxide, and then fractionally distilled *in vacuo* to remove carbon dioxide, water and iodine impurities. Two consecutive batches of deuterium iodide were always prepared;

the first served only to flush out the entire sample-handling glassware and cells, prior to actual spectrometric measurements which were conducted only on the second batch in order to maintain isotopic purity. Pressure measurements were made with mercury manometers with an accuracy of 0.05 kN m^{-2} in the range 1-2 kN m^{-2}.

Spectrophotometric measurements were made of the sample vapours contained in a 100-mm fused silica cell, using a Cary model 14 and a Unicam SP800C. Spectral slit widths were 40-80 cm^{-1}. Only curves obtained on the SP800C instrument were used for analysis, for which the linear wavenumber presentation proved advantageous. Checks of absorbance accuracy and determination of maximum extinction coefficient of HI only were made on the Cary instrument. Spectra from the SP800C were measured with instrument calipers at 500 cm^{-1} intervals, and the results converted to extinction coefficients with simple programmes.

TABLE 1.—EXTINCTION COEFFICIENTS OF HYDROGEN AND DEUTERIUM IODIDES

	ϵ	
ν (cm^{-1})	HI	DI
32 000	2	—
32 500	3	—
33 000	4	—
33 500	5.5	2
34 000	8	3
34 500	11	5
35 000	15	8
35 500	20.5	12.5
36 000	27	16.5
36 500	35.5	22.5
37 000	45.5	31.5
37 500	55	41
38 000	68.5	53
38 500	82	66
39 000	97.5	79.5
39 500	113.5	97
40 000	130	115
40 500	145	134
41 000	159.5	154
41 500	174.5	172.5
42 000	185	190
42 500	195	205
43 000	203.5	217.5
43 500	210	227.5
44 000	216.5	236
44 500	219.5	240
45 000	220	241
45 500	219.5	240
46 000	217.5	238
46 500	215.5	234
47 000	209.5	223.5
47 500	202.5	215
48 000	197	205
48 500	191	195.5
49 000	184.5	185
49 500	177.5	171
50 000	170.5	161
50 500	163.5	151
51 000	156.5	140
51 700	148	122.5
52 200	144	114

RESULTS

The experimental results consist of values of extinction coefficients ε at wavenumbers ν from the detectable onset of absorption, about 31 000 cm^{-1} with the path length and pressures employed, to the limit of the range of the spectrometers, about 52 000 cm^{-1}. These results are listed in table 1, and the spectra are illustrated in fig. 1. The absolute wavenumber accuracy is ± 50 cm^{-1}. The absolute accuracy of the extinction coefficients is limited to ± 5 % by accuracy of the pressure measurements. The relative accuracy of extinction coefficients is ± 2 %, except at the extremes of the range of absorption. Agreement with previously published reliable results,[1, 2, 5] is within the stated absolute accuracy. Other maximum extinction coefficients of 213.4 for HI and 247.8 for DI have also been mentioned.[6] The extinction coefficients are properly designated decadic molar extinction coefficients, and thus have units of l. mol^{-1} cm^{-1}. The area under the absorption curves can be approximated by the product of the maximum extinction coefficient and twice the half-width at half maximum intensity on the small wavenumber side, to produce an estimate of the oscillator strength, $(1.1 \pm 0.1) \times 10^{-2}$, the same for both isotopic molecules. Of potential interest to photochemists, the values of the extinction coefficients at the mercury emission line wavenumber, 39 413 cm^{-1}, are 110 ± 5 for HI and 90 ± 5 for DI.

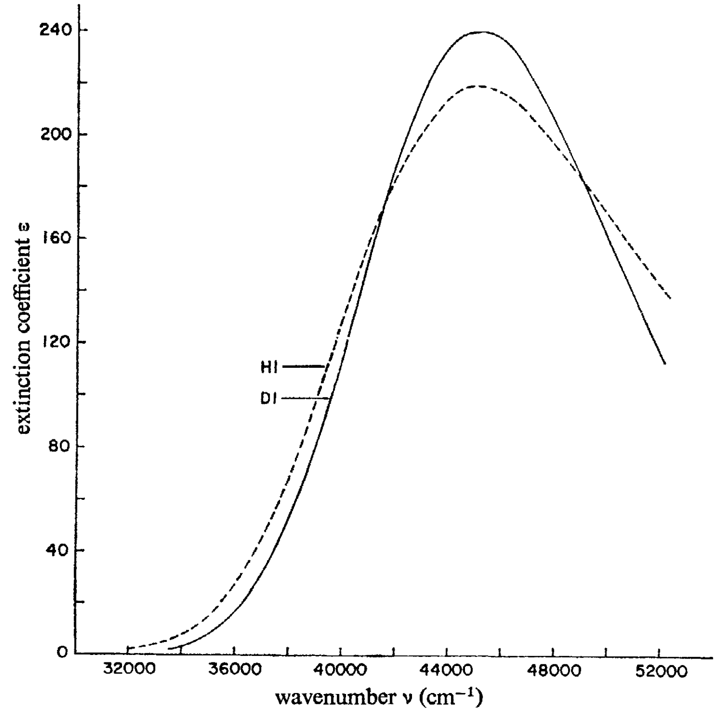

FIG. 1.—Electronic continua of hydrogen and deuterium iodide vapours at 294 K.

TREATMENT

The present objective is to calculate potential curves for the excited state of hydrogen and deuterium iodides reached from the near ultraviolet absorption. Comparison of potential curves of isotopic molecules in an unstable state using the present method demands accurate potential curves for the ground state and vibrational wavefunctions. For the former, potential curves calculated from vibration-rotational spectroscopic data suffice, and wavefunctions in a usable analytic form have become available [3] with an accuracy near the limitations of the Born–Oppenheimer approximation. These wavefunctions $\psi_{(v,J)}(x)$ are based on the Dunham potential function [7]:

$$V(x) = a_0x^2(1+a_1x+a_2x^2+a_3x^3+a_4x^4 \ldots),$$

in which the coefficients a_i are determined from vibration-rotational spectroscopic parameters, listed in table 2. To take account of rotational effects, the quantities x and a_i ($i = 0,1,2,3$) can be formulated [3] to include a dependence on the rotational

TABLE 2.—SPECTROSCOPIC PARAMETERS OF HI AND DI REQUIRED FOR COMPUTATION OF POTENTIAL CONSTANTS, ETC.

quantity	HI	DI	units
ω_e	2 309.53 [a]	1 640.14 [a]	cm^{-1}
$\omega_e x_e$	39.98 [a]	20.16 [a]	cm^{-1}
B_e	6.512 8 [b]	3.284 0 [a]	cm^{-1}
α_e	0.172 8 [b]	0.061 42 [a]	cm^{-1}
γ_e	0.000 69 [c]	0.000 176 [d]	cm^{-1}
r_e	160.9	160.9	pm
zero-point energy	1 145.5	815.4	cm^{-1}
D_e, dissociation energy	25 707 [e]	25 677	cm^{-1}

[a] data from L. H. Jones, *J. Mol. Spectr.*, 1957, **1**, 179.

[b] data from P. Arcas, C. Hauseler, C. Joffrin, C. Meyer, N. van Thanh and P. Barchewitz, *App. Optics*, 1963, **2**, 909.

[c] estimated from the relation given by W. R. Jarmain, *Canad. J. Phys.*, 1960, **38**, 217.

[d] estimated from the value for HI using the isotope relation [15]

[e] derived from data given by Herzberg.[6]

quantum number J. For HI and DI vapours at 295 K, the most populated rotational levels are $J = 4$ and $J = 5$, respectively, of $v = 0$. Potential constants in this case are listed in table 3. Symbols used in this paper have the usual spectroscopic significance.[8] $\gamma = (B_e/a_0)^{\frac{1}{2}} = (2B_e/\omega_e)$. The dimensionless variable is given by $x = (r-r_e)/r_e$, representing a reduced form of instantaneous internuclear separation.

TABLE 3.—POTENTIAL CONSTANTS USED FOR HI ($J = 4$) AND DI ($J = 5$)

	HI	DI	units
a_0	204 747.9	204 785.3	cm^{-1}
a_1	−2.567 8	−2.556 6	
a_2	4.150 8	4.078 9	
a_3	−5.134	−4.842	
a_4	(5.48) [a]	(5.48) [a]	
γ	0.005 648 4	0.004 009 0	
Y_{00}	0.74	0.33	cm^{-1}

[a] derived from extrapolation in hydrogen halide series (R. H. Tipping, private communication); value is not corrected for J-dependence.

The potential energy curve for the ground state of HI obtained from the parameters in table 3 is compared in fig. 2 with Morse [9] and harmonic oscillator potential curves constructed from parameters appropriate for HI. The Dunham potential function (including terms up to x^4) produced a curve very similar to the Morse function at reduced separations $x < +0.2$, but the curve is then subject to a catastrophic increase, which, however, does not affect calculations based on the Dunham potential near the minimum of the curve about $x = 0$.

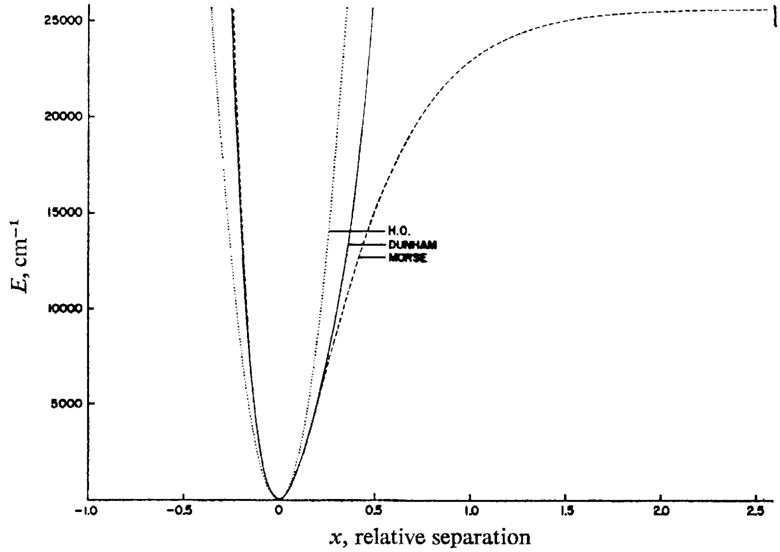

FIG. 2.—Potential energy curves of the ground electronic state of hydrogen iodide according to harmonic oscillator, Dunham and Morse potential functions based on spectroscopic parameters.

The wavefunctions [3] derived for the most populated rotational levels of the ground vibrational state ($v = 0$) of HI and DI are illustrated in fig. 3. These curves are really probability functions, that is, the square of the eigenfunctions. The amplitude functions for HI and DI are respectively:

$$\psi^{\mathrm{HI}}_{(0,4)}(x) = 2.7138 \exp [1.28235x - 88.6353x^2 + 75.7743x^3 - 55.3790x^4 + 34.0135x^5];$$

$$\psi^{\mathrm{DI}}_{(0,5)}(x) = 2.9649 \exp [1.27689x - 124.8182x^2 + 106.2529x^3 + 76.2280x^4 + 42.8729x^5].$$

Integrals involving these amplitude functions, being exponential functions of polynomials, have the property [3] of possibly diverging outside the range of interest ($-1 < x < 2$), but this feature does not affect their use in the following calculations. Comparison of these probability functions with those of the corresponding harmonic oscillator functions:

$$\psi^{\mathrm{HI}} = 2.7409 \exp [-88.6536x^2];$$

$$\psi^{\mathrm{DI}} = 2.9859 \exp [-124.8586x^2],$$

as also illustrated in fig. 3, clearly reveals the effects of anharmonicity (a_1, a_2, a_3, $a_4 \neq 0$). As expected, the anharmonic curves are displaced toward more positive $x(r > r_e)$, and are slightly skewed in the same direction.

The construction of unstable state potential curves is straightforward under a few assumptions,[8] now to be outlined. The Born–Oppenheimer approximation allows us to consider nuclear motion separately from electronic motion and thus to construct potential curves in the first place. The total intensity of the electronic transition, or oscillator strength, is proportional to the square of a matrix element. The latter involves an integral of the total wavefunctions ψ_T of combining states and an electric moment or transition dipole moment M:

$$\int \psi'_T M \psi''_T d\tau.$$

The Born–Oppenheimer approximation permits us to factor the electronic and vibrational wavefunctions. (Rotational wavefunctions are entirely neglected here).

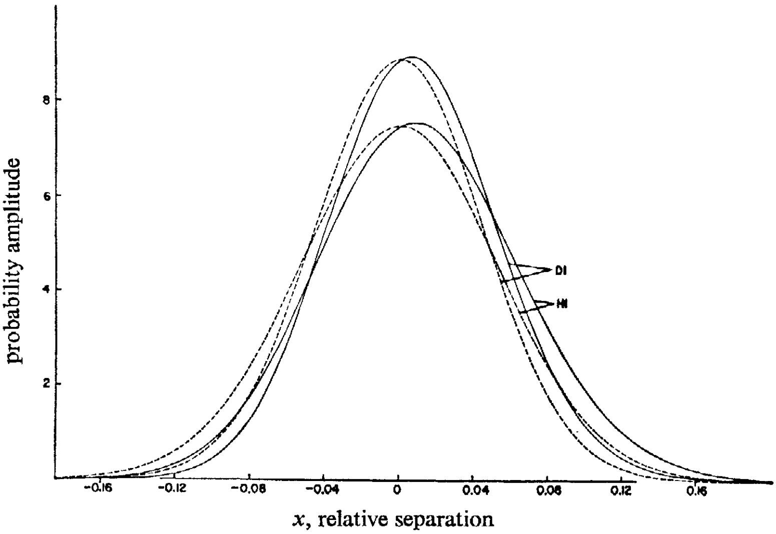

FIG. 3.—Harmonic (dashed line) and anharmonic (solid line) vibrational probability amplitude functions (normalized) of HI and DI. The resemblance between the relation of the two full (or two dashed) curves here and the two spectral curves in fig. 1 should be noted.

Assuming the electronic transition moment M to be a slowly varying function of x permits the integral over electronic coordinates to be considered a constant quantity, affecting only the total or integrated intensity of the electronic transition. Assuming the vibrational eigenfunction of the repulsive upper state to be approximated by a δ-function, of non-zero amplitude for each energy V at only one small region of x on the potential curve of the unstable state, permits reduction of the integral to a readily calculable value of a function at each value of x. The result of all these assumptions is that the intensity of absorption at a particular wavenumber depends on the square of the ground-state vibrational wavefunction multiplied by a wavenumber factor appropriate to a transition in absorption:

$$\varepsilon(\nu) \propto \nu[\psi''_{(v,J)}(x)]^2.$$

The justification for considering only one particular rotational level in the ground state is discussed later.

COMPUTATIONAL PROCEDURE

To remove the wavenumber factor in the above expression, extinction coefficients divided by wavenumber were listed in the second column of a table opposite the appropriate wavenumber. Listed in the third column, relative reduced extinction coefficients were prepared by dividing all reduced extinction coefficients (ε/ν) by the maximum value in the second column. Then a comparison was made of the values of these relative reduced extinction coefficients with a graph of unnormalized vibrational probability functions. The maximum in the relative reduced extinction coefficient column (1 exactly) was taken to correspond to the maximum of the probability function. So it was possible to associate similar magnitudes of relative reduced extinction coefficient with relative vibrational probability function, and thus to relate a value of x to an absorption wavenumber. These values of x were listed in the fourth column. When the transition wavenumbers are increased by the zero-point energy and the rotational energy (relative to that for $J = 0$) of the supposed initial level ($J = 4$ or 5), these wavenumbers can be entered in the fifth column. Then the corresponding values of x and energy V (expressed in wavenumber units throughout this article) in the fourth and fifth columns of this table constitute the co-ordinates of points denoting the repulsive potential curves. Thus the series of points in fig. 4 were generated.

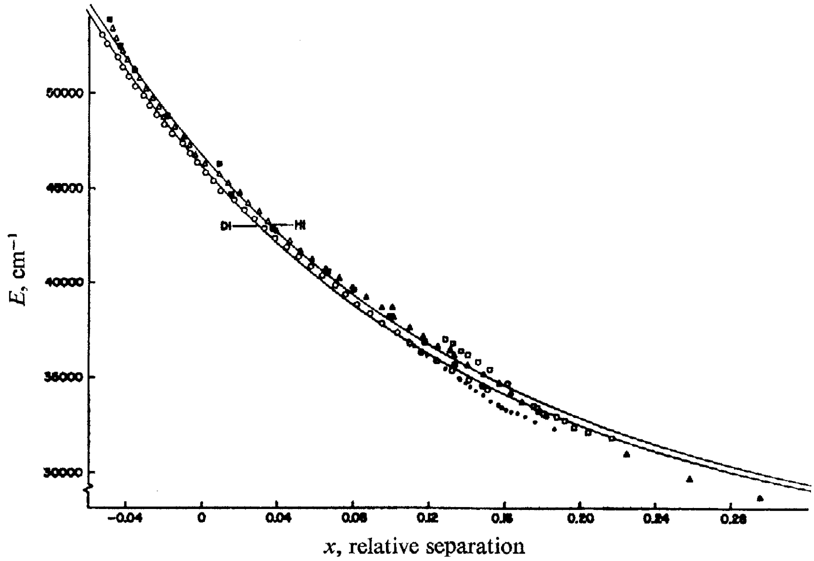

FIG. 4.—Points and derived curves for potential energy of HI and DI in the repulsive excited electronic state reached from their electronic continua in fig. 1. Open circles and triangles are derived from spectra of this work, for DI and HI respectively. Closed circles and open squares are similarly from the article of Bates, Halford and Anderson,[2] whereas the closed squares and closed triangles, both for HI, are derived from spectra of Huebert and Martin [4] and Goodeve and Taylor [1] respectively.

DISCUSSION

Processing the spectral data of table 1 for HI and DI, as just described, led to two apparently distinct series of points in fig. 4, which seemingly indicates that the two isotopic molecules have distinctly different repulsive potential curves for their unstable states. To provide further points, reliable absorption coefficient data taken from the literature [1, 2, 5] were similarly processed. Where no maxima were clearly observed [1, 2] in the measured spectra, the maxima for HI and DI obtained in this study were employed. Although there is considerable scatter in regions of points from more than one source, the basic feature of two distinctly different series remains. For the HI data of Huebert and Martin,[5] the points were obtained independently of any intensity results of this study; they are generally in good agreement with the present results.

For the points obtained from the author's data, the following least squares fits to exponential decays were derived (standard deviations are indicated):

$$V_{\mathrm{HI}} = 25\,707+(20\,982\pm 84)\exp[(-5.350\pm 0.049)x]$$

$$V_{\mathrm{DI}} = 25\,677+(20\,474\pm 45)\exp[(-5.485\pm 0.032)x].$$

For all points of HI and DI (taken separately), the corresponding equations are:

$$V_{\mathrm{HI}} = 25\,707+(21\,345\pm190)\exp[(-5.70\pm0.07)x]$$

$$V_{\mathrm{DI}} = 25\,677+(20\,541\pm106)\exp[(-5.82\pm0.05)x].$$

The greater magnitudes of the numerical coefficients in the exponents reflect the apparently greater slopes of the points obtained from the earlier work. The equations for these groups of points by themselves are:

$$V_{\mathrm{HI}} = 25\,707+(28\,308\pm600)\exp[(-7.5\pm0.1)x]$$

(Goodeve and Taylor [1])

$$V_{\mathrm{HI}} = 25\,707+(29\,704\pm1070)\exp[(-7.5\pm0.2)x]$$

(Bates, Halford and Anderson [2])

$$V_{\mathrm{DI}} = 25\,677+(24\,383\pm396)\exp[(-7.1\pm0.1)x]$$

(Bates, Halford and Anderson [2]).

On the other hand the equation obtained for points derived from data of Huebert and Martin [5] alone is in good agreement with the equation for the author's points:

$$V_{\mathrm{HI}} = 25\,707\pm(21\,145\pm159)\exp[(-5.53\pm0.1)x].$$

For comparison, the equation obtained by Goodeve and Taylor [1] in their early work has been transformed to the same form as those above, as follows:

$$V_{\mathrm{HI}} = 25\,610+20\,400\exp[(-2.06)x].$$

Points pertaining to small wavenumber absorption fall away from the calculated curve, just as in fig. 4. In all cases for the newly derived equations, constraints have been applied to force asymptotic approach, at large x, to the energies of the separated atoms in their ground states, H or D, 1^2S and I, $5^2P_{\frac{3}{2}}$. The value [8] of 25 707 cm^{-1} has been taken as the dissociation energy D_e of HI. Then the 30 cm^{-1} difference in D_e for DI represents the difference in ionization energies of H and D.[10]

From the statistical analysis, the coefficients of x in the exponents, -5.350 ± 0.049 and -5.485 ± 0.032 (also 5.53 ± 0.1), are probably not distinct, but the pre-exponential factors differ by several standard deviations, $20\,982\pm84$ and $20\,474\pm45$. Thus there seems to be an isotope effect in these repulsive potential energy curves. The energy difference between the two curves alluded to above for the equations of which there are the smallest standard deviations, varies from 300 to 500 cm^{-1} in the defined region. If the curves are really distinct, then this could either be an electronic isotope effect for repulsive states, or be regarded as a partial failure of the Born–Oppenheimer approximation.[8] Confirmation awaits more accurate spectroscopic data, for a more probable source of the discrepancy is inaccuracy which enters the calculations in many forms. Inaccuracy in the maximum extinction coefficient does not matter as only relative values are used (at least within the author's sets of points); non-linearity of the absorbance scale of the spectrophotometer within twice the checked tolerances should not cause the observed effect since the spectra of HI and DI, illustrated in fig. 1, are basically very similar, and the conditions during the recording were as nearly similar as could be arranged. Indeed the basic reason for the two distinct repulsive curves is the fact that the maxima of the continua of HI and DI have apparently the same wavenumbers. The shift of the DI spectrum to greater wavenumbers by about 500 cm^{-1} required to bring the two repulsive curves into coincidence is not perceptible in the present electronic spectra. The very magnitude of the discrepancy, by comparison with the hydrogen atom-deuterium atom shift of 30 cm^{-1}, indicates that experimental causes, not the breakdown of the Born–Oppenheimer approximation, are responsible.[11] whence the requirement for more accurate data. In any case, the defining of a shift of 330 cm^{-1} in the maximum of a band with a half-width of 12 000 cm^{-1} poses considerable difficulty even in principle, although Gordus and Caughey [6] seem to have measured a shift of maximum from 44 470 cm^{-1} for HI to 44 684 cm^{-1} for DI.

The analytic form of the vibrational wavefunctions with an included J-dependence[3] has an inherent accuracy near that of the Born–Oppenheimer approximation. To ensure that the effects are attributable to a partial failure of this approximation, a further iteration to derive even more accurate wavefunctions is required.[3] Such corrections will have only a minor effect compared to the discrepancy obtained here. A more important source of error involves the Dunham potential constants from which the wavefunctions are computed. As indicated in table 3, two different sets for HI and DI have resulted from the use of experimental spectroscopic parameters as in table 2. A consequence is that the ground electronic state potential functions appear to differ slightly. The Dunham constants a_i are very sensitive to experimental error in spectroscopic parameters,[12] and the wavefunctions are also sensitive to cumulative error in the a_i. Improvement of the spectroscopic parameters by two orders of magnitude or more would be necessary to check whether the ground state potential curves are significantly different. There is some precedent for an isotope effect in potential curves of bound electronic states,[13] and electronic isotope shifts in electronic transitions between bound states have already been explained.[14] The latter effect is much smaller than that here observed for HI and DI.

The approximations in the theoretical procedure have already been mentioned. To use a wavefunction more complex than a single δ-function at each point along the repulsive curves would greatly complicate the computations. However the effect of using accurate wavefunctions for the repulsive state is being investigated, and the indication is that the δ-function is a reasonable approximation (R. H. Tipping, personal communication). Undoubtedly the neglect of variation of electronic transition moment with internuclear separation over the large range of x, corresponding to the large wavenumber range in which the continuous absorption is measurable, may cause considerable error.

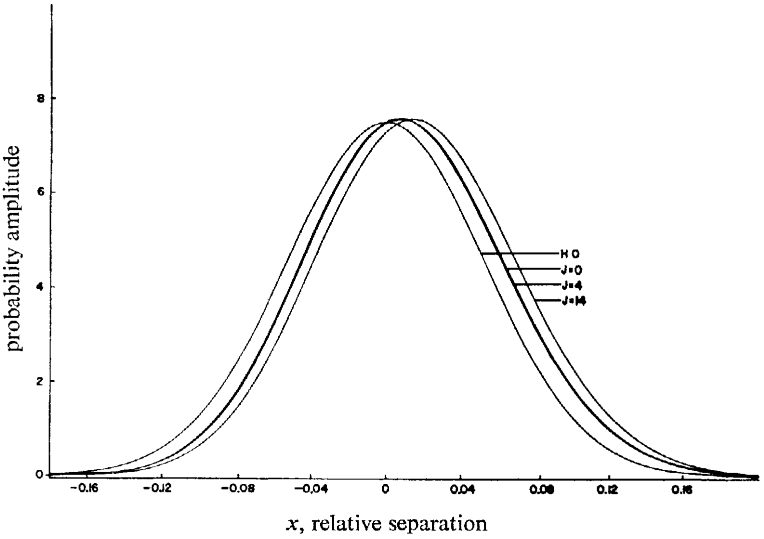

FIG. 5.—Vibrational probability amplitude functions for HI in $v = 0$ of the ground electronic state; harmonic oscillator, and anharmonic oscillator curves for $J = 0$, 4, and 14 are shown.

The use of only the most populated rotational level as the origin of the electronic transitions, deserves comment. (Effects due to equilibrium thermal population of $v = 1$ levels should be undetectable within present measurements of the absorption). The curves of fig. 5 illustrate for HI the J-dependence of the probability functions.[3] With increasing J, the maxima of the curves move to greater x, the shift being quadratic in J; the breadth of the curves at half maximum height also increases slightly. The three curves for the anharmonic oscillator wavefunctions apply to $J = 0$, the pure vibrational case; $J = 4$, most populated level; and $J = 14$, which has population less than one per cent that of $J = 4$ at the temperature of measurements. Some ninety per cent of HI molecules have $J<8$; for these molecules, despite the quadratic dependence on J, the $J = 4$ curve probably represents an acceptable approximation. Effects for $J<4$ will be compensated partially by effects for $J>4$, except in the region of large x for which absorption by molecules with large J (and eventually $v = 1$) becomes important. The result of neglect of these large-J levels causes points at large x to fall below the curves, as can be observed in fig. 4. If more accurate spectroscopic parameters become available, repetition of these calculations including the weighted effect of all populated rotational levels would be worth while.

Only one electronic transition has been assumed to occur in the region of spectroscopic measurements. There is no evidence for another potential curve related to dissociation to hydrogen or deuterium atoms and to excited iodine atoms [2] in the $5^2P_{\frac{1}{2}}$ state which lies 7603 cm^{-1} above $^2P_{\frac{3}{2}}$. However the deviation of points from the HI curve near 54 000 cm^{-1} may be connected with the onset of absorption associated with the next electronic transition.[5, 14]

With regard to the intensity of the electronic transition, the estimated oscillator strength 0.011 is in fact not *much less* than 0.010 as estimated by Mulliken.[16] As far as can be estimated from the data of Huebert and Martin [5], the oscillator strength HBr is also 0.011. The ratio of the maximum extinction coefficients for HI and DI in the continua ought to be very close to the square of the ratio of the normalization factors of the vibrational amplitude functions, which is 0.84. The experimental ratio is 0.91. Inaccuracy in pressure measurement is sufficient to account for the discrepancy.

Finally a comment might prove useful concerning the nature of Y_{00} in the formulation of the vibration-rotational energy levels according to Dunham [7]:

$$E(v,J) = \sum_{l,j=0} Y_{lj}(v+\tfrac{1}{2})^l J^j (J+1)^j$$

First of all, the isotope relation attributed to Kemble,[17]

$$Y^i_{lj}/Y_{lj} = (\mu/\mu^i)^{(l+2j)/2}$$

does not practically apply to Y_{00}. Second, the physical significance of Y_{00} is an addition to zero-point energy beyond that arising from a non-rotating anharmonic oscillator. The terms constituting Y_{00}[8, 14]

$$Y_{00} = B_e/4+\alpha_e\omega_e/(12B_e)+\alpha_e^2\omega_e^2/(144B_e^3)-\omega_e x_e/4$$

indicate the physical meaning. The first term, $B_e/4$, is obviously a purely rotational contribution to zero-point energy. This aspect seems not to have been remarked previously. The next two terms are concerned with vibration-rotational interactions, and the last term is a further anharmonicity contribution. As a fraction of the rotational spacing, $2B$, the rotational term $B_e/4$ is only one-eighth, whereas the harmonic vibrational zero-point energy, $\omega_e/2$, is half the vibrational spacing. In fact Y_{00} is a very small correction as the effect of the various terms is partially to cancel one another.

For instance, typical values of Y_{00} in ground states are $\sim$1 cm^{-1} for hydrides, half of that for deuterides, except $\sim$9 and $\sim$3 cm^{-1} for diatomic hydrogen and deuterium respectively, and much smaller for heavier diatomic molecules.

I am grateful to Dr. R. H. Tipping for instructive comments.

[1] C. F. Goodeve and A. W. C. Taylor, *Proc. Roy. Soc. A*, 1936, **154**, 181.

[2] J. R. Bates, J. O. Halford and L. C. Anderson, *J. Chem. Phys.*, 1935, **3**, 415, 431.

[3] R. M. Herman, R. H. Tipping and S. Short, *J. Chem. Phys.*, 1970, **35**, 595.

[4] J. K. Cashion and D. R. Herschbach, *J. Chem. Phys.*, 1964, **40**, 2358.

[5] B. J. Huebert and R. M. Martin, *J. Phys. Chem.*, 1968, **72**, 3046.

[6] A. A. Gordus and D. A. Caughey, *Am. Chem. Soc. Abstract V* 139, Autumn, 1965.

[7] J. L. Dunham, *Phys. Rev.*, 1932, **41**, 721.

[8] G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* (second ed., Van Nostrand, Princeton, 1959).

[9] P. M. Morse, *Phys. Rev.*, 1929, **34**, 57.

[10] C. E. Moore, *Atomic Energy Levels*, N.B.S. Circular 467, vol. 1 (National Bureau of Standards, Washington, 1949).

[11] R. E. Weston, *Tetrahedron*, 1959, **6**, 31.

[12] R. Tipping and R. M. Herman, *J. Chem. Phys.*, 1966, **44**, 3112.

[13] I. Sandeman, *Proc. Roy. Soc.* (Edin.), 1939, **59**, 1.

[14] P. R. Bunker, *J. Mol. Spectr.*, 1968, **28**, 422.

[15] S. G. Tilford, M. L. Ginter and A. M. Bass, *J. Mol. Spectr.*, 1970, **34**, 327.

[16] R. S. Mulliken, *J. Chem. Phys.*, 1940, **8**, 382.

[17] R. S. Mulliken, *Phys. Rev.*, 1925, **25**, 126.