

Dissociation Energy and Vibrational Terms of Ground-State ($X^1\Sigma_g^+$) Hydrogen*

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In an attempt to elucidate the discrepancy between the theoretical and experimental dissociation energies of H_2 , accurate binding energies and term differences have been computed for the 15 vibrational levels using the Kolos and Wolniewicz clamped-nuclei potential with its various corrections. The results suggest possible interpretations of the discrepancy. In one of these an extrapolation method is introduced which combines experimental term differences with computed binding energies for the uppermost levels to yield the dissociation energy; this result is in accord with the experimental value of Herzberg and Monfils. The effect of uncertainties in the values of the natural constants is considered. Apparent inconsistencies between previously computed vibrational energies are explained.

I. INTRODUCTION

Considerable attention has been devoted to the problem of accurate *ab initio* computation of the dissociation energy and vibrational terms of the various isotopic forms of hydrogen. For the best studied case of ground-state H_2 , a discrepancy of some 4 cm^{-1} exists between Herzberg and Monfils' possible experimental value of the dissociation energy,¹ $36\,113.6(\pm 0.3)\text{ cm}^{-1}$, and the "fully corrected" theoretical value of Kolos and Wolniewicz (KW),² $36\,117.4\text{ cm}^{-1}$. This discrepancy is especially serious since the theoretical value is a variational result (except for -0.2 cm^{-1} due to the radiative correction) and is thus expected to be a lower bound. A serious but less publicized discrepancy exists between the observed³ and computed^{2,4-9} vibrational term differences; the experimental $\Delta G_{v+1/2}$ values (accurate to $\pm 0.05\text{ cm}^{-1}$) differ with the calculated ones by an accumulated total of $\sim 4\text{ cm}^{-1}$ over the 15 vibrational levels. It is not clear whether or not these two discrepancies are related.

In the present study, the computed vibrational spectrum is used as a measure of the local accuracy of the theoretical potential. Corresponding to two of the possible interpretations of the source of the disagreement between theory and experiment, two empirical "correction functions" to the KW potential are presented for consideration.

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¹ G. Herzberg and A. Monfils, *J. Mol. Spectry*, **5**, 482 (1960). The value given corresponds to the $B'(^1\Sigma_u^+)$ assignment of the upper state of the observed transition. Their alternate assignment, the $C(^1\Pi_u)$ state corresponding to $D_0 = 36\,113.0(\pm 0.3\text{ cm}^{-1})$, is made very unlikely by *ab initio* computations of the potential for this state which show it to possess a barrier with a maximum of $\sim 100\text{ cm}^{-1}$.

² (a) W. Kolos and L. Wolniewicz, *Phys. Rev. Letters* **20**, 243 (1968); (b) *J. Chem. Phys.* **49**, 404 (1968).

³ G. Herzberg and L. L. Howe, *Can. J. Phys.* **37**, 636 (1959).

⁴ J. K. Cashion, *J. Chem. Phys.* **45**, 1037 (1966).

⁵ L. Wolniewicz, *J. Chem. Phys.* **45**, 515 (1966).

⁶ J. D. Poll and G. Karl, *Can. J. Phys.* **44**, 1467 (1966).

⁷ T. G. Waech and R. B. Bernstein, *J. Chem. Phys.* **46**, 4905 (1967).

⁸ D. F. Zetik and F. A. Matsen, *J. Mol. Spectry*, **24**, 122 (1967).

⁹ F. M. Greenawald and A. S. Dickinson, *J. Mol. Spectry*, (unpublished).

II. METHOD

A. Vibrational Eigenvalues as a Local Test of the Accuracy of a Potential

For any given diatomic internuclear potential, exact bound-state eigenfunctions and eigenvalues may be efficiently computed.⁸⁻¹² In addition, it may be shown (see Appendix A) that a given eigenvalue is especially sensitive to small changes in the potential in the immediate neighborhood of its two turning points $R_1(v)$ and $R_2(v)$. For the higher levels, this dependence is increasingly weighted towards the outer turning point $R_2(v)$. The inverse problem of deriving a potential "correction function" which would remove the difference between computed and observed energies may also be solved uniquely, provided that the maximum error in the original theoretical potential is everywhere reasonably small. The results in Appendix A indicate that this inversion is possible for H_2 if the KW potential^{2,13,14} is accurate to better than about 10 cm^{-1} over the range of the turning points of the 15 vibrational levels. That this is the case is shown by the approximate ($\pm 5\text{ cm}^{-1}$) agreement between its computed eigenvalue spectrum and experiment.

B. Method of Comparing Computed and Observed Eigenvalues

The customary comparison of computed and observed vibrational-rotational energies via the quantity $T_0(v, J) = [T(v, J) - T(0, 0)]$ (e.g., Ref. 7) is undesirable here, since it assumes that the absolute value of the energy computed for the ground ($v=0, J=0$) state agrees with experiment. A better approach would be to compare the binding energies¹⁵ $E_b(v)$. However, the $\pm 0.3\text{ cm}^{-1}$ uncertainty in the experimental D_0

¹⁰ J. W. Cooley, *Math. Computation* **15**, 363 (1961).

¹¹ J. K. Cashion, *J. Chem. Phys.* **39**, 1872 (1963).

¹² H. Harrison and R. B. Bernstein, *J. Chem. Phys.* **38**, 2135 (1963); **47**, 1884 (1967), Erratum.

¹³ W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3663 (1964).

¹⁴ W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965).

¹⁵ Throughout, the "binding energy" of a given level is the energy difference between that level and the asymptote of the potential, while "dissociation energy" refers to the binding energy of the $v=0, J=0$ level.

would yield experimental binding energies with uncertainties too great for the current analysis.

The present approach combines the accurate *observed* vibrational spacings (reported to 0.01 cm^{-1}) with the precise binding energies *computed* from the best available potential. As is illustrated in Fig. 1, the experimental and computed levels for a given v are matched, and the computed binding energy is added to the experimental vibrational energy to yield an "apparent" ground-state dissociation energy, defined $D_0(v) = [E_b(v) + T_0(v, 0)]$. If the theoretical potential were exact, the curve of $D_0(v)$ vs v would be horizontal at the true dissociation energy since the difference between each $D_0(v)$ and the true D_0 is merely the error in the computed $E_b(v)$. Otherwise, $[D_0(v+1) - D_0(v)]$ is the negative of the error in the computed $\Delta G_{v+1/2}$ so that a $D_0(v)$ curve is effectively a second-order Birge-Sponer plot with unknown ordinate zero. It will be seen (in Sec. IV.B) that under certain conditions this type of plot may be used in an extrapolation procedure to yield the "true" D_0 .

III. CALCULATIONS

A. Computation of Vibrational Energies

Vibrational eigenvalues were obtained by solving the radial Schrödinger equation numerically using a modified version of the Cooley-Cashion program.^{10,11} (See Appendix B for a comparison of this with the Harrison and Bernstein¹² and Zetik and Matsen^{8,9} methods.)

The integration is performed on the equation ex-

pressed in the reduced form

$$(d^2Y/dz^2) + B_z[E^* - V^*(z)]Y = 0, \quad (1)$$

where $z = R/R_m$, $Y(z) = z\chi(R)$, $E^* = E/\epsilon$, $V^*(z) = V(R)/\epsilon$, and $B_z = 2\mu\epsilon R_m^2/\hbar^2$; the parameters R_m and ϵ are arbitrary scaling factors (usually chosen close to R_e and D_e). The reduced mass used for most of the computations was that for two protons. Despite the contrary arguments of Cashion,⁴ this appears to be the correct choice of mass since Eq. (1) describes the motion of the nuclei in an effective potential arising from the field of the electrons. The total potential $V(R)$ includes the usual clamped-nuclei and centrifugal potentials, and for most of the calculations it contained the relativistic and nuclear motion (adiabatic) corrections as well. The integration was carried out over the interval $0.4 \leq R \leq 10$ a.u., and the increment used (the "mesh size") was 0.007 a.u. Expanding the interval or decreasing the mesh size affected the eigenvalues negligibly (i.e., by $< 0.01\text{ cm}^{-1}$).

The required physical constants are all collected in the factor $B_z = 3.64566 \times 10^3 \mu\epsilon R_m^2 (\pm 0.5 \times 10^{-3} \%)$,¹⁶ where μ is the reduced mass in "unified" atomic mass units ($^{12}\text{C} = 12$), and ϵ and R_m are both expressed in atomic units. The effect on the eigenvalues of error in the physical constants is tempered by the radial kinetic-energy factor $T_K = [E - V(z)]$ with which B_z is combined in Eq. (1). To a first approximation, a given error in B_z , say ΔB_z , introduces an error

$$\Delta E_v = -(\Delta B_z/B_z) \langle v | T_K | v \rangle \quad (2)$$

to the computed energy for level v . The kinetic energies $\langle v | T_K | v \rangle$ (e.g. those later presented in Table III) cause the effect of error in the physical constants to diminish for levels approaching either the top or the bottom of the well, while reaching a maximum about $\frac{3}{4}$ of the way up. An adjustment of the electron mass^{16,17} changing B_z by one standard error ($\pm 0.5 \times 10^{-3} \%$) affects the H_2 vibrational energies for levels 6–11 (where $\langle v | T_K | v \rangle$ is greatest) by $\sim \mp 0.06\text{ cm}^{-1}$, while affecting the $v=0$ energy by less than $\mp 0.01\text{ cm}^{-1}$.

B. Effect of Interpolation on Eigenvalue Precision

The KW clamped-nuclei potential for H_2 was reported at 87 points in the interval $0.4 < R < 10$ a.u., while ~ 1500 points are needed in the numerical integration. The interpolation between the given points is therefore very critical, and indeed appears to be the major source of eigenvalue imprecision.

¹⁶ With μ , ϵ , and R_m expressed in unified atomic mass units ($^{12}\text{C} = 12$) and atomic units, the numerical part of B_z is just $2/m_e$, where m_e is the electron mass in atomic mass units. The uncertainty is the standard error in the best known value of m_e .¹⁷

¹⁷ E. R. Cohen and J. W. DuMond, *Rev. Mod. Phys.* **37**, 537 (1965).

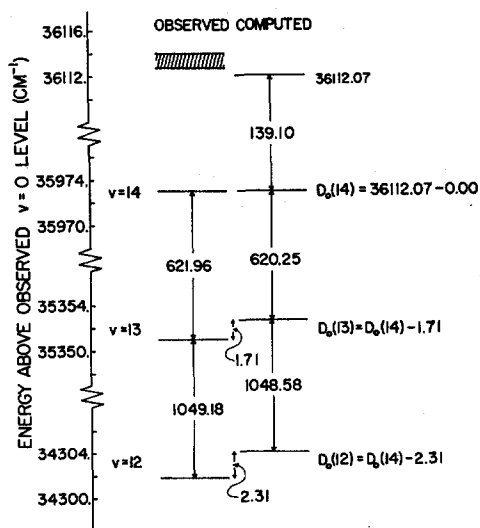


FIG. 1. Derivation of $D_0(v)$ values by matching computed and observed levels at $v=14$. The number $36\ 112.07$ [i.e., $D_0(14)$] would equal the dissociation energy if the computed value of $E_b(14)$ were exactly correct. Here the $E_b(v)$ were obtained for the relativistic, adiabatic KW potential (using nuclear reduced mass).

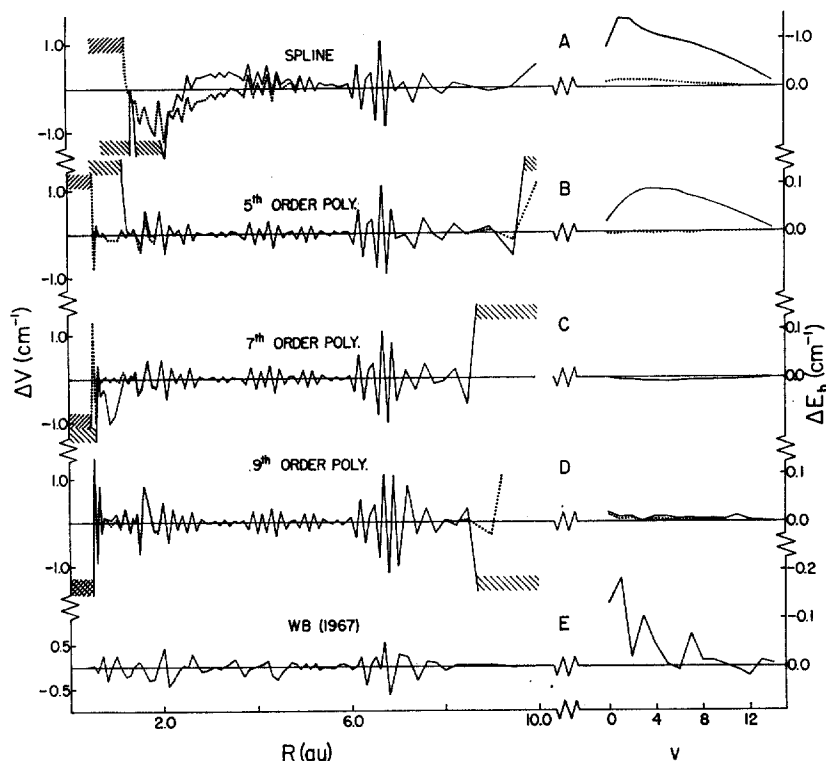


FIG. 2. Comparison of effects of diverse interpolation schemes on the potential and its eigenvalues. $\Delta V = (V_{\text{KW}} - V_{\text{int}})$; $\Delta E_b = \{E_b[\text{seventh-order polynomial over } (R^2V)] - E_b(\text{other})\}$. \cdots Interpolation over $\{R^2V_{\text{KW}}(R_i)\}$; $—$ Interpolation over $\{V_{\text{KW}}(R_i)\}$. Note the several different scales on the right ordinate. Case A uses eight point third-order spline fits; Case B uses fifth-order polynomials; Case C uses seventh-order polynomials; Case D uses ninth-order polynomials; and Case E uses the analytic formula of Ref. 7.

The accuracies of several interpolation schemes were tested by omitting in turn each of the computed KW clamped-nuclei points, and comparing the i th omitted value $V_{\text{KW}}(R_i)$ to that obtained by interpolation over the remaining data, $V_{\text{int}}(R_i)$. All of the methods used were piecewise fits which selected an equal number of the given points from either side of the desired value. It is clear that interpolating over $\{R_i^2V_{\text{KW}}(R_i)\}$ (as suggested by Poll and Karl⁶) rather than over $\{V_{\text{KW}}(R_i)\}$ significantly improves the results. The interpolations giving rise to the differences $\Delta V_i = [V_{\text{KW}}(R_i) - V_{\text{int}}(R_i)]$ in Fig. 2 used 85 of the KW¹⁴ points, the entries at $R=1.400$ and 1.401 a.u. being omitted.¹⁸ Figure 2 also shows the effect on the computed eigenvalues of using different interpolation schemes, the binding energies obtained via the piecewise seventh-degree polynomial interpolation over $\{R_i^2V_{\text{KW}}(R_i)\}$ being used as a reference. The precision of the best results is $\sim \pm 0.02$ cm^{-1} . Combining this interpolation imprecision with the uncertainty in B_7 shows that the accuracy with which

¹⁸ The KW points at 1.400 and 1.401 a.u. were omitted from the interpolations since their inclusion yielded an anomalously high density of data in this region, producing erroneously large errors (large ΔV_i) at adjacent points interpolated using the higher-order (seventh- and ninth-order) polynomials.¹⁹ The removal of these two values changed the potential yielded by the piecewise seventh-order-polynomial interpolation enough to increase the binding energy of the $v=0$ level by 0.035 cm^{-1} , though it affected higher levels by less than 0.01 cm^{-1} .

¹⁹ The Lagrangian interpolation subroutine of R. N. Zare [University of California Radiation Laboratory Report, UCRL-10925, 1963, (unpublished)] was used for all of our piecewise polynomial interpolations.

our computed eigenvalues "reflect" the KW potential lies within the limits ± 0.03 cm^{-1} (for $v=0$) and ± 0.08 cm^{-1} (for $v=6-11$).

The differences ΔV_i in Parts A-D of Fig. 2 are, however, considerably larger than the actual error in $V(R)$ carried into the eigenvalue calculation, since the interpolated potential actually used is constrained to pass through all the KW points. In Part E, on the other hand, the differences ΔV_i are the actual errors in the analytical potential²⁰ of Ref. 7.

C. The Total Potential $V(R)$

In the present work a smooth clamped-nuclei potential was obtained in the interval $0.45 \leq R < 9.0$ a.u. using a series of seventh-order-polynomial fits¹⁹ over $\{R_i^2V_{\text{KW}}(R_i)\}$ to 85 of the 87¹⁸ KW (1965) points. At the ends of this range where the numerical interpolation becomes least accurate (see Fig. 2) the potential was extrapolated analytically. For $R < 0.45$ a.u. it was approximated by a function of the form $V(R) = A/R^B + C$, where the three constants were determined by fitting the function to the three KW points at smallest R . For $R \geq 9.0$ a.u. the potential was represented by a theoretical five-term analytical expression derived from perturbation theory. The C_6 , C_8 , C_{10} , and

²⁰ The analytic fit of Ref. 7 [using the method of G. E. Forsythe, J. Soc. Ind. Appl. Math. 5, 74 (1957)] of the whole potential to a single polynomial expression of 32nd degree is of course not constrained to give precise agreement with all 87 reported KW¹⁴ values.

TABLE I. Difference between KW clamped-nuclei-potential^a and perturbation-theory results.^b

R (a.u.)	7.0	7.2	7.6	7.8	8.0	8.25	8.5	9.0	9.5	10.0
$E_{\text{PtbN}} - E_{\text{KW}} (\text{cm}^{-1})$	2.26	1.27	0.72	0.53	0.24	0.11	0.13	-0.15	-0.11	0.11
$-E_{\text{KW}} (\text{cm}^{-1})$	41.56	31.47	19.05	14.97	11.74 ^c	8.87	6.89	4.05	2.66	2.00

^a Reference 14. ^b Reference 21. ^c Reference 22.

C_{11} inverse-power potential constants and the exponential expression for the exchange contribution were taken from Hirschfelder and Meath.²¹ Table I shows the agreement between the KW potential and the above extrapolation over the range $R=7-10$ a.u.²² Since these long-range (for $9 \leq R \leq 10$ a.u.) and short-range (for $0.40 \leq R < 0.45$ a.u.) extrapolations are applied to R values outside the range of the classical turning points of the highest vibrational level [$R_1(14) \cong 0.78$ a.u. and $R_2(14) \cong 6.2$ a.u.], any errors they introduce are expected to produce a negligible effect on the eigenvalues.

Series of third-order polynomials were used to interpolate between the KW values of the relativistic and nuclear motion (adiabatic) corrections. Beyond the range of their computations, the relativistic correction at large R and the adiabatic correction at small R were extrapolated using analytic functions,²³ errors in which would at worst introduce errors of $\sim 0.03 \text{ cm}^{-1}$ in the computed eigenvalues for levels above $v=11$. In addition, the adiabatic correction at large R was approximated by an exponential fitted to pass through the last two values at finite R and decaying to the asymptote. Although other workers^{2,5,6} have used significantly different extrapolations, the exponential tail seems most reasonable in view of its excellent qualitative agreement (see Fig. 3) with the correction computed from the expressions derived by Van Vleck.²⁴ Inaccuracy in this

²¹ J. O. Hirschfelder and W. J. Meath, *Advan. Chem. Phys.* **12**, 3 (1967).

²² It has been pointed out by P. R. Certain, J. O. Hirschfelder, W. Kolos, and L. Wolniewicz [*J. Chem. Phys.* **49**, 24 (1968)] that a calculation using an improved basis set of electronic wavefunctions lowers the KW¹⁴ clamped-nuclei energy at 8.0 a.u. by 0.15 cm^{-1} to -11.74 cm^{-1} . This improved value was used in Table I. It should be remembered that the estimated rounding errors in the single-precision KW clamped-nuclei results were stated to be $\pm 0.1 \text{ cm}^{-1}$.

²³ The relativistic correction at large R was approximated by an exponential fitted to the last two KW points at finite R and decaying to the asymptote, a distance of 0.42 cm^{-1} . The adiabatic correction for $R < 0.6$ a.u. was extrapolated by an exponential fitted to pass through the two KW points at smallest R (absolute values were used in this fit; cf. values expressed relative to the asymptote). Since the latter extrapolation begins at $0.6 \text{ a.u.} < R_1(14) \cong 0.78 \text{ a.u.}$, it could introduce only negligible errors to the computed eigenvalues.

²⁴ J. H. Van Vleck, *J. Chem. Phys.* **4**, 327 (1936). Although the Wang electronic wavefunction used by Van Vleck is relatively inappropriate at small R , it becomes increasingly suitable as R increases through the region in question and is almost exact at the asymptote. Values of the Wang function's variational exponential parameter were derived by extrapolating over the values reported by J. O. Hirschfelder and J. W. Linnett [*J. Chem. Phys.* **18**, 130 (1950)]. Equation (51) in this paper by Van Vleck contains an extraneous factor of b^2 .

extrapolation could at worst introduce errors of $\sim 0.5 \text{ cm}^{-1}$ in the eigenvalues computed for levels above $v=10$.

D. The Nonadiabatic Correction

The nonadiabatic correction to the eigenvalues arising from the coupling of the ground state to excited electronic states was approximated by a formula derived by Van Vleck²⁴ (and recently used by Poll and Karl⁶). This treatment starts with a second-order perturbation energy, and by using an Unsöld approximation and summing over complete sets of vibrational and electronic states yields the following expression:

$$\Delta E(v) = -\frac{4}{\nu_0} \langle v | T_K | v \rangle \times \left\langle \Phi_e(r_e, R) \left| -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \right| \Phi_e(r_e, R) \right\rangle_{\bar{R}_v}, \quad (3)$$

where ν_0 is the Unsöld energy, T_K is the radial kinetic energy, and the third factor is an expectation value over the electronic coordinates of the ground state, evaluated with the nuclei separated by $\bar{R}_v = \langle v | R | v \rangle$. This factor is one of those contributing to the adiabatic correction, for which Van Vleck had derived an analytic expression. The value initially chosen for the Unsöld energy, $\nu_0 = 1.35 \times 10^6 \text{ cm}^{-1}$, was derived²⁵ from consideration of sums of a different type of matrix element and may be somewhat inaccurate. It may be more correct, too, to replace ν_0 by $\nu_v = [\nu_0 - T_0(v, 0)]$. The expectation values $\langle v | T_K | v \rangle$ are readily evaluated from the radial wavefunctions which are obtained from the eigenvalue calculation.

IV. RESULTS

A. Sources of Disagreement of Previous Computed Eigenvalues

Several calculated sets of vibrational eigenvalues for the KW potential have already been published.⁴⁻⁸ Waech and Bernstein⁷ compared those results supposedly based on the clamped-nuclei potential and found discrepancies of up to 12 cm^{-1} . Upon further study it appears that these differences result from the use of slightly different potentials and physical constants. The most prominent single effect is due to the

²⁵ J. H. Van Vleck and A. Frank, *Proc. Natl. Acad. Sci. (U.S.)* **15**, 539 (1929).

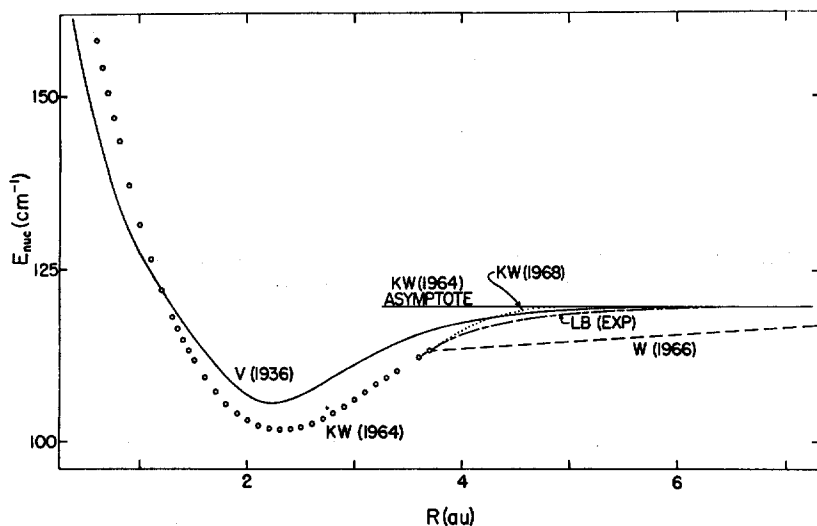


FIG. 3. Nuclear motion correction. O are the 1964 KW points; V(1936) comes from the Van Vleck formulation²¹; KW(1968), 1968 KW² graphical extrapolation; LB(EXP), present authors' exponential extrapolation; and W(1966), Wolniewicz's linear extrapolation.

TABLE II. $D_0^{(i)}(v)$ results.^a

v	$i=1$			$i=2$		$i=3$		$i=4$			$i=5$		
	$D_0(v)$	$D_0(v)$	$\Delta_{W(2)}$	$D_0(v)$	$\Delta_{PK(2)}$	$D_0(v)$	Δ_C	Δ_{WB}	$D_0(v)$	$\Delta_{W(5)}$	$\Delta_{PK(5)}$		
0	36 118.0	36 117.9	0.0	36 117.4	0.0	36 112.8	0.0	0.2	36 112.2	0.0	-1.0		
1	18.1	17.0	0.1	16.4	0.1	11.5	0.0	0.4	09.8	0.0	-1.1		
2	18.2	16.2	0.1	15.6	0.1	10.5	-0.1	0.4	07.9	0.0	-1.1		
3	17.7	14.9	0.1	14.3	0.1	09.1	-0.5	0.6	05.7	0.1	-1.0		
4	17.6	14.0	0.1	13.4	0.1	08.3	-0.9	0.6	04.2	0.1	-1.3		
5	17.3	13.3	0.2	12.7	0.2	07.7	-1.6	0.6	03.0	0.1	-1.9		
6	17.0	12.4	0.2	11.8	0.2	07.2	-2.8	0.7	02.0	0.1	-3.0		
7	16.6	11.7	0.2	11.2	0.2	07.0	-4.5	0.7	01.5	0.1	-4.6		
8	16.2	11.2	0.2	10.6	0.3	07.0	-7.5	0.6	01.4	0.1	-7.6		
9	15.8	10.7	0.2	10.2	0.3	07.3	-11.9	0.6	01.7	0.1			
10	15.3	10.3	0.3	09.9	0.3	07.7		0.6	02.3	0.1			
11	14.7	10.1	0.8	09.7	0.2	08.3		0.5	03.4	0.2			
12	13.9	10.1	1.8	09.7	-0.2	08.9		0.4	04.7	0.2			
13	13.4	10.6		10.3	-0.6	10.0		0.3	06.9				
14	13.6	12.2		12.1	-0.4	12.0		0.2	10.5				

^a Δ is the amount (in cm^{-1}) by which the previously reported $E_0(v)$ [and hence $D_0(v)$] exceeds that computed here for the same case. Δ_W compares present results to those of Wolniewicz²; Δ_{PK} compares with Poll and Karl⁶; Δ_C compares with Cashion⁴; and Δ_{WB} compares with

Waech and Bernstein.⁷ The parameter i denotes a particular choice of potential and reduced mass: $i=1$: relativistic, adiabatic, μ atomic; 2: nonrelativistic, adiabatic, μ nuclear; 3: relativistic, adiabatic, μ nuclear; 4: clamped nuclei, μ atomic; and 5: clamped nuclei, μ nuclear.

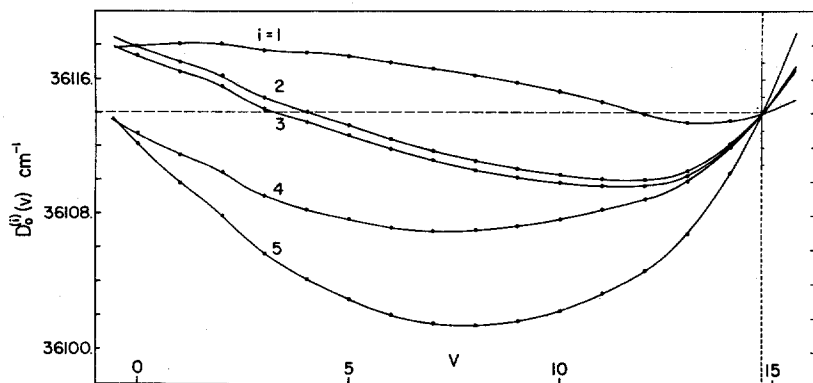


FIG. 4. $D_0^{(i)}(v)$ curves plotted from the results in Table II. The curves were derived by piecewise interpolation with series of second-order polynomials. The "bumps" at $v=2$ are explained in Sec. IV.A.

use of different values for the reduced mass; in some of the studies^{4,7} the atomic rather than the nuclear masses were used.²⁶ The various possible cases have now been analyzed and sets of apparent dissociation energies $D_0^{(i)}(v)$ have been computed for five of them ($i=1, \dots, 5$). These are plotted in Fig. 4 and are compared to the previously published results in Table II. The causes of the remaining differences Δ between the present results and those reported previously for the same case, are given below.

The largest differences, Δ_C and $\Delta_{PK(i=5)}$, both arise from their use of the earlier (1964), less-accurate versions¹³ of the clamped nuclei potential.²⁷ In $\Delta_{W(2)}$ and $\Delta_{PK(3)}$ the escalating deviance above $v=0$ corresponds to the use of extrapolations of the nuclear motion correction differing markedly from that used here. The linear extrapolation of Wolniewicz⁵ ($\Delta_{W(2)}$) is shown by Fig. 3 to be much too coarse.

The remainder of $\Delta_{W(2)}$ and $\Delta_{PK(3)}$ as well as $\Delta_{W(5)}$ and much of Δ_{WB} may be quantitatively explained in terms of the effect of error in the physical constants, discussed in Sec. III.A. Wolniewicz,⁵ Poll and Karl,⁶ and Waech and Bernstein⁷ used values of B_x which were all too large²⁸ by, respectively, $1.3 \times 10^{-3} \%$, $1.2 \times 10^{-3} \%$, and $8.7 \times 10^{-3} \%$. Upon substituting these differences into Eq. (2) along with the kinetic energies from Table III, most of the given Δ 's are explained, except that portion of Δ_{WB} which Fig. 2 shows to be due to the Waech and Bernstein interpolation procedure. Some small errors in the earlier work are also due to the use by Waech and Bernstein⁷ and Poll and Karl⁶ of integration meshes two and three times larger than used here.

The differences between results calculated using the same potential but slightly different reduced masses (e.g., compare cases $i=1$ and 4, respectively, to $i=3$ and 5) are also quantitatively explained in terms of the effect of the difference in reduced mass on the B_x factor. Changing from nuclear to atomic reduced mass increases B_x by 0.0545%, which when substituted in Eq. (2) yields the observed differences.

Since none of the curves in Fig. 4 are flat, none of the sets $i=1, \dots, 5$ yield vibrational spectra in agreement with experiment; also, the relativistic adiabatic μ -nuclear ($i=3$) curve which should be best appears worse than the corresponding μ -atomic case ($i=1$).

²⁶ We are indebted to Dr. T. G. Waech for bringing this to our attention.

²⁷ Poll and Karl⁶ ($\Delta_{PK(3)}$) used the energies computed with 54-term electronic wavefunctions over the whole of the interval $0.4 \leq R \leq 3.7$ a.u., and Cashion⁴ (Δ_C) added to these the more accurate potential energies reported in the more restricted interval about the minimum $0.55 \leq R \leq 2.0$ a.u.

²⁸ With the Cohen and DuMond¹⁷ constants as a reference, Wolniewicz⁵ used a reduced mass which is $\sim 1.3 \times 10^{-3} \%$ too large, Poll and Karl⁶ used a value of the Bohr radius $0.6 \times 10^{-3} \%$ too large, and Waech and Bernstein⁷ used values of Planck's constant and the Bohr radius which were, respectively, $6. \times 10^{-3} \%$ too small and $1. \times 10^{-3} \%$ too large.

TABLE III. Results from the 1968 relativistic adiabatic KW potential.^a

v	$E_0(v)^b$	$D_0(v)$	$\langle v T_K v \rangle$	$\Delta E(v)$	$\Delta E'(v)$
0	36 117.54	36 117.5	1 079.	-0.65	-0.65
1	31 955.44	16.6	3 040.	-1.83	-1.89
2	28 028.78	15.8	4 770.	-2.89	-3.07
3	24 332.61	15.0	6 275.	-3.82	-4.19
4	20 863.88	14.2	7 555.	-4.59	-5.17
5	17 621.61	13.5	8 609.	-5.15	-5.97
6	14 607.10	12.8	9 427.	-5.67	-6.74
7	11 824.31	12.1	9 996.	-6.03	-7.35
8	9 280.42	11.4	10 292.	-6.27	-7.82
9	6 986.80	10.7	10 278.	-6.33	-8.07
10	4 960.09	10.3	9 904.	-6.16	-8.01
11	3 223.20	10.1	9 098.	-5.69	-7.53
12	1 808.15	10.0	7 754.	-4.84	-6.49
13	759.48	10.5	5 713.	-3.51	-4.76
14	139.16	12.1	2 755.	-1.65	-2.24

^a All energies are in cm^{-1} . The kinetic energies are approximately the same as for cases $i=1, \dots, 5$ in Table II. $\Delta E(v)$, the nonadiabatic correction to the energy, is the negative of the correction to the binding energy and to $D_0(v)$. The unprimed nonadiabatic correction was evaluated using ψ_0 and corresponds to Curve B in Fig. 5, while $\Delta E'(v)$ was evaluated using the adjusted Unsöld energies ν_s and yielded Curve C.

^b As indicated in Secs. III.A and III.B, these eigenvalues reflect the KW potential with accuracies ranging from $\pm 0.03 \text{ cm}^{-1}$ to $\pm 0.08 \text{ cm}^{-1}$. They may not be directly compared to the most recent KW results² since the latter did not include the relativistic correction in the effective potential.

The addition of the nonadiabatic correction improves the situation, but it will be shown that results for the theoretically best case still do not yield the observed vibrational ladder.

All of the curves in Fig. 4 exhibit an anomalous "bump" at $v=2$ which is due to small errors in the Herzberg and Howe³ energies for $v=1$ and 2.²⁹ These have been remeasured³⁰⁻³² and the most recent data³² give $T_0(1, 0) = 4161.181 \text{ cm}^{-1}$ and $T_0(2, 0) = 8087.01 \text{ cm}^{-1}$. Substituting these values for those of Herzberg and Howe increases all $D_0(1)$ values in Table II and Fig. 4 by 0.04 cm^{-1} , and decreases all $D_0(2)$ values by 0.10 cm^{-1} , completely removing the apparent anomaly.

B. The Dissociation Energy and the Vibrational Spectrum

In the following work the Herzberg and Howe³ vibrational ladder is used with the addition of the corrected experimental values of $T_0(1, 0)$ and $T_0(2, 0)$ given above. The eigenvalues reported below were computed (using the nuclear reduced mass) from the relativistic adiabatic potential described in Sec. III.C, with

²⁹ The Herzberg-Howe results³ are a composite of three sets of nonoverlapping experimental data: their own Lyman-band measurements which place the levels $v=3$ to 14 relatively, B. P. Stoicheff's [Can. J. Phys. **35**, 730 (1957)] Raman data for the $v=0-1$ transition, and G. Herzberg's [Can. J. Res. **A28**, 144, (1950)] pioneering quadrupole absorption measurements of the $v=0-2$ and $0-3$ transitions (as reinterpreted by Stoicheff).

³⁰ C. H. Church, Ph.D. thesis, University of Michigan, Ann Arbor, Mich., Rept. UMRI-2609-3-T, 1959 (unpublished).

³¹ U. Fink, T. A. Wiggins, and D. H. Rank, J. Mol. Spectry. **18**, 384 (1965).

³² J. V. Foltz, D. H. Rank, and T. A. Wiggins, J. Mol. Spectry. **21**, 203 (1966).

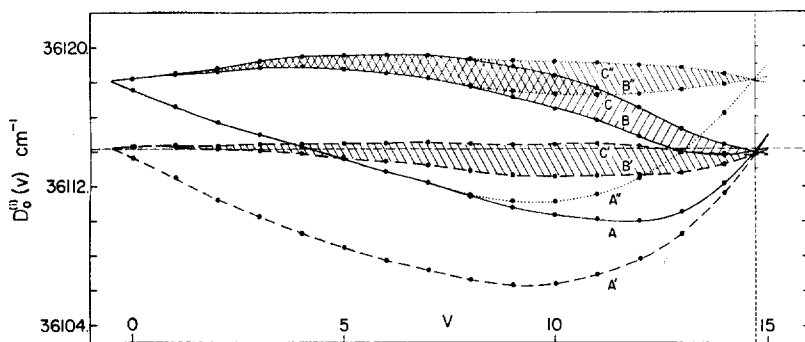


FIG. 5. $D_0(v)$ curves from best KW-(1968) potential. Curve A corresponds to Column 3 in Table III; B and C include the nonadiabatic corrections from Columns 5 and 6, respectively; the shaded area is a measure of the uncertainty in the nonadiabatic correction. A' , B' , and C' , and A'' , B'' , and C'' , respectively, illustrate the effect on Curves A, B and C of adding corrections Δ' and Δ'' in Fig. 6 to the effective potential.

one modification; KW's 1965 clamped-nuclei results in the interval $1.0 \leq R \leq 3.2$ a.u. have been replaced by their more recent² double-precision results.³³

In Appendix A it is shown that eigenvalues computed for the highest vibrational levels are most sensitive to the accuracy of the potential just inside their respective outer turning points. This is confirmed by the convergence of the several curves in Fig. 4 at $v=14.71(\pm 0.02)$.³⁵ This occurs because the relativistic and adiabatic corrections monotonically approach their asymptotes over the range of the $R_2(v)$ for the highest levels, thus causing the difference between the several effective potentials to approach zero in this region. It occurs despite the fact that these effective potentials differ significantly (by between +20 and -17 cm^{-1} relative to the asymptote) over the region between the turning points.

By definition, $D_0(v)$ is equal to the true dissociation energy if the computed binding energy for level v is correct. For the highest levels this is equivalent to requiring that the potential be accurate in the neighborhood of $R_2(v)$. Since the computed potential is exact at $R=\infty$, $D_0(14.71)$ must equal the true dissociation energy, though the question may be raised whether the "true" value of $D_0(14.71)$ may be derived from a simple extrapolation on a graph such as Fig. 4. This is the case if the clamped-nuclei potential exhibits its true asymptotic behavior in the interval spanned by the $R_2(v)$'s for the highest levels, or more precisely, if the error in the clamped-nuclei potential monotonically approaches zero in this interval. With this as-

³³ Unfortunately the new values are reported only at 17 of the 29 original points on this interval. In order to minimize the interpolation error, the difference between the old and new results was assumed to vary continuously (except for the expected discontinuities³⁴ at 1.6 and 2.0 a.u.) and improved values were obtained at all 29 original points. Omitting the thus improved points affected the eigenvalues by as much as 0.05 cm^{-1} .

³⁴ An error in the 1965 KW point at $R=1.6$ a.u. has been pointed out by C. L. Beckel and J. P. Sattler [J. Mol. Spectry. 20, 153 (1966)], while the discontinuity at $R=2.0$ a.u. is expected since this is the point at which the 1965 KW results switched from an 80-term to a 54-term electronic wavefunction. The discontinuities at these points are also evidenced by the relatively large amplitude, in their neighborhoods, of the interpolation error functions in Fig. 2.

³⁵ This uncertainty in the point of intersection is the average deviation of the results of several different numerical extrapolation schemes.

sumption, the present results yield $D_0(14.71) = D_0 = 36114.1(\pm 0.2)$ ³⁵ cm^{-1} . This value agrees within the mutual uncertainties with the experimental value,¹ $D_0 = 36113.6(\pm 0.3)$ cm^{-1} .

We have recomputed eigenvalues from the relativistic adiabatic potential (including the improved 1968 clamped-nuclei results) and added in the nonadiabatic correction, evaluating the latter using both Van Vleck and Frank's²⁵ Unsöld energy ν_0 , and the present "adjusted" values ν_0 (Sec. III.D). These results, given in Table III, yield the three solid curves (A, B, and C) in Fig. 5. Since the nonadiabatic correction is the same for the several cases in Table II as it is here, Fig. 5 shows that its addition does not affect the values of the intersection point. The distance between Curves B and C is a measure of the uncertainty in the nonadiabatic correction, though it does not represent a bound. The radiative correction to the energies is not discussed here since Wolniewicz⁵ has derived a bound on its magnitude which is smaller than the uncertainty in the nonadiabatic correction.

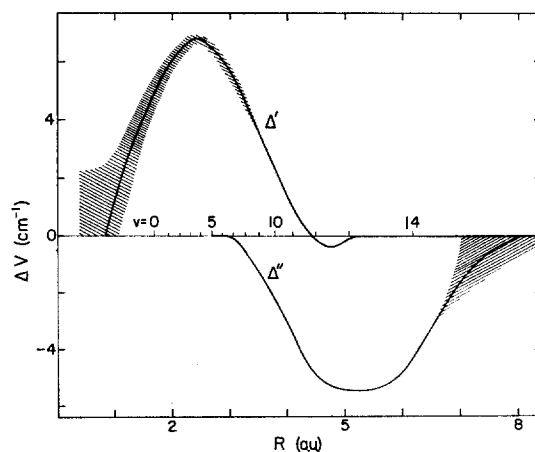


FIG. 6. Empirical "correction functions" for the KW potential. Addition of either of these functions, Δ' or Δ'' , to $V(R)$ induced a flattening of the initially computed nonadiabatic $D_0(v)$ curves (B and C) in Fig. 5, corresponding to better agreement between computed and observed vibrational spacings. The shaded regions are an estimate of the nonuniqueness of the inversion of the primed and double-primed results in Fig. 5 which yielded Δ' and Δ'' , respectively. The v designations on the abscissae denote the outer turning points $R_2(v)$.

Since neither the adiabatic nor the nonadiabatic results reproduce the observed vibrational term differences within reasonable limits, we have derived two possible "correction functions" for the potential, curves Δ' and Δ'' in Fig. 6. The addition of these functions to the effective potential causes the eigenvalue calculation to yield the $D_0(v)$ curves A', B', and C' (corresponding to Δ'), and A'', B'', and C'' (corresponding to Δ'') in Fig. 5. Δ' and Δ'' are uniquely determined by their respective $D_0(v)$ curves to within the indicated uncertainties. The nonuniqueness of Δ' at small R arises since a given change in one of the lowest vibrational eigenvalues could be induced by changes in the potential at either or both turning points (see Appendix A). The uncertainty in the tail of Δ'' [for $R > R_2(14) \cong 6.2$ a.u.] arises since the eigenvalues are only slightly affected by small changes in the potential beyond the outer turning point; however, it seems likely that it should quickly approach zero for $R > 8$ a.u. where the KW potential agrees with perturbation theory results (see Table I).

V. DISCUSSION

Although the addition of the nonadiabatic correction yields better agreement with experiment (compare B and C in Fig. 5, with A), the computed vibrational ladder is still elongated relative to the experimental one by an accumulated total of 4 cm^{-1} (two orders of magnitude greater than the uncertainty in the experimental data). This implies that the theoretical potential for $R \leq R_2(14)$ is stretched relative to the exact curve by about 4 cm^{-1} , approximately the disagreement between the experimental and computed dissociation energies; of course the two disagreements may not be related.

If the two effects mentioned above are related, any questioning of the accuracy of the experimental dissociation energy is equally a questioning of the experimental term differences involving an accumulated total of 4-cm^{-1} error. Alternately, if the experimental dissociation energy is assumed to be correct [agreeing with $D_0(14.71)$], the clamped-nuclei potential must be too deep by $\sim 4 \text{ cm}^{-1}$. In this case the relative flatness of Curves B and C in Fig. 5 over the range $v=0-8$ merely indicates that the bowl of the KW^{2,13,14} potential has essentially the correct shape. The correction to the potential suggested by this interpretation is curve Δ' in Fig. 6, and its "beneficial" effect on the eigenvalues is shown by Curves A', B', and C' in Fig. 5. These nonadiabatic results (Curves B' and C') yield reasonable agreement with both the observed vibrational spectrum and dissociation energy. However, this interpretation requires a reasonable accuracy ($\sim \pm 0.5 \text{ cm}^{-1}$) for the KW potential at large R ($R \cong 6$ a.u.), and KW point out² that this part of the adiabatic potential is expected to be less accurate than that in the vicinity of equilibrium. On the other hand, the good agreement with perturbation-theory results (see Table I) for

$R > 8$ a.u. implies that the KW potential is indeed quite accurate (e.g., $\pm 0.5 \text{ cm}^{-1}$) in this region,³⁶ which makes it seem unlikely that it be 4 cm^{-1} too shallow at $R=6$ a.u.

Another interpretation, believed by the present authors to be less likely, would treat the disagreements of the dissociation energy and of the vibrational levels as unrelated. The former would be due to some as yet undiscovered error in the experimental work or its interpretation,¹ the latter to error in the clamped-nuclei potential at large R . This error (curve Δ'' in Fig. 6) would not exhibit its asymptotic behavior (i.e., would not monotonically approach zero) over the range of $R_2(v)$'s for the highest levels, thus invalidating the extrapolation method suggested in Sec. IV.B.

In a recent paper which also discusses the present problem,² KW arrived at a "final" theoretical value for $D_0(0) = E_b(0)$, of 36117.4 cm^{-1} . We see here that the inclusion of the nonadiabatic correction which is necessary for reducing the disagreement with the experimental vibrational term differences increases this to 36118.0 cm^{-1} [our nonadiabatic $D_0(0)$ evaluated from Table III, plus the radiative correction³⁷] which increases the disagreement with the experimental value to 4.4 cm^{-1} . The variational contribution to this theoretical dissociation energy is 36117.54 cm^{-1} . This is a rigorous upper bound³⁸ to the exact ground-state energy of a fictitious system described by the KW adiabatic Hamiltonian plus the Breit-Pauli approximation to the relativistic correction. However, since this simplified total Hamiltonian cannot be expected to accurately describe H_2 , the above quantity need not be an upper bound to the experimental dissociation energy. Thus the correction function Δ' in Fig. 6 does not violate the variational principle if, for example, it is interpreted as an improvement in the relativistic correction. In this case, the total relativistic correction to the ground-state energy would be 6 cm^{-1} .

It should be emphasized that the present paper does not resolve the question of the discrepancy between the experimental dissociation energy of H_2 and $E_b(0) = D_0(0)$. On the basis of the evidence at hand it cannot be decided which of the values $D_0(0) = 36118.0 \text{ cm}^{-1}$ or $D_0(14.71) = 36114.1 \text{ cm}^{-1}$ best represents the "theoretical" dissociation energy. While the former is the quantity customarily considered, the latter has the advantage of being determined mainly by the potential at large R where the relativistic and adiabatic corrections, whatever their accuracy elsewhere, are approaching their asymptotic values.

³⁶ This is further suggested by the results in Footnote 22 which show that the use of an improved electronic-wavefunction basis set only affected the clamped-nuclei potential at 8.0 a.u. by 0.15 cm^{-1} .

³⁷ J. D. Garcia, Phys. Rev. **147**, 66 (1966).

³⁸ This assumes that replacing the 54-term electronic wavefunction with which the adiabatic and Breit-Pauli relativistic corrections were calculated,¹³ by the 100-term wavefunction used in the most recent clamped-nuclei calculations,² would not significantly change the corrections.

Although an accurate relativistic treatment of this problem is beyond the scope of present methods, the results presented here suggest two feasible calculations which would shed some light on the question of the H₂ dissociation energy. The first is a more accurate recalculation of the clamped-nuclei potential in the interval ($3 \lesssim R \lesssim 7$ a.u.), where Δ'' (see Fig. 6) is nonzero; the second, a more accurate treatment of the non-adiabatic correction, such as that suggested by modern variational techniques.

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APPENDIX A: LOCALIZATION OF THE "POTENTIAL DEPENDENCE" OF A VIBRATIONAL EIGENVALUE

The high sensitivity of an eigenvalue E_v to the potential near its turning points may be qualitatively explained by considering the effect on the semiclassical JWKB phase integral

$$I_v = 2 \frac{\mu}{\hbar^2} \int_{R_1(v)}^{R_2(v)} [E_v - V(R)]^{1/2} dR = (v + \frac{1}{2})\pi$$

of a small shift in the potential (ΔV) over a narrow interval ($\Delta E_v'$) about a given value of $E_v' = [E_v - V(R)]$. To a first approximation, the change is

$$\Delta I_v = -\frac{\mu}{\hbar^2} \frac{\Delta V}{(E_v')^{1/2}} \frac{\Delta E_v'}{|dV/dR|}$$

for $E_v' / |\Delta V| > 1$; it reaches a maximum of

$$(\mu/\hbar^2) |\Delta V|^{1/2} (\Delta E_v' / |dV/dR|)^{-1}$$

(for $\Delta V < 0$) at the classical turning point, where $\Delta E_v' / (-\Delta V) \rightarrow 0$. An analogous result for $E_v' \rightarrow 0$ can be evaluated for the somewhat more complicated case $\Delta V > 0$. Since $I_v = (v + \frac{1}{2})\pi$, ΔV must induce a change in E_v which varies as $[(E_v')^{1/2} |dV/dR|]^{-1}$, but approaches a finite limit at the turning points where $E_v' = 0$. For the higher levels, the $|dV/dR|$ factor shifts this sensitivity almost exclusively to the outer turning point $R_2(v)$.

The potential dependence of the eigenvalues as described above is modulated somewhat by the oscillating nature of the exact radial wavefunction. This effect may be seen by considering the perturbation theory expression for the eigenvalue change due to the given potential shift, $|Y_v|^2 \Delta V (\Delta E_v' / |dV/dR|)^{-1}$. The term involving the wavefunction $|Y_v|^2$ shifts the potential dependence inward from the turning point to the region where it has its outermost maximum.

These considerations were illustrated by direct computations, by observing the effect on the H₂ vibrational eigenvalues of localized shifts in the relativistic, adiabatic KW potential.^{13,14} The results, given in Table IV, indicate that error in an eigenvalue indeed reflects error in the potential in the neighborhood of its turning points, especially the outer one; this is of course contingent on the assumption that the maximum absolute error in the potential is everywhere relatively small. If this condition is not satisfied, the effect on the eigenvalues of inaccuracy in $V(R)$ midway between the turning points will no longer be distinguishable from that of error in their immediate proximity.

APPENDIX B: COMPARISON OF BOUND-STATE EIGENVALUE PROGRAMS

The Cooley-Cashion^{10,11} (C-C) method was quantitatively compared to that of Harrison and Bernstein¹² (HB) and found to be faster by a factor of ~ 5 . One large difference between the two lies in their respective methods of estimating the improvement in the trial eigenvalue while iteratively converging on the exact result. In the HB program the increment of improvement decreases by a factor of $\frac{1}{2}$ in successive steps, while with the predictor-corrector formula of C-C the necessary improvement decreases by about two orders of magnitude with each iteration. The other major difference between these methods is that the Runge-Kutta integration of HB requires three to four times as much computation as the Numerov method of C-C to span a given interval for the same increment.

Both of the above methods proceed by direct numerical integration of the radial Schrödinger equation. Zetik and Matsen,⁸ on the other hand, expand the

TABLE IV. Effect on H₂ vibrational eigenvalues of changing the potential over a given interval.^a

v	E_b	A	B	C
0	36 118.	0.0	0.0	0.0
2	28 029.	0.0	0.0	0.0
4	20 864.	0.0	0.0	0.2
6	14 607.	0.0	0.0	0.3
7	11 824.	-0.1	0.0	0.3
8	9 280.	-0.6	0.2	0.4
9	6 987.	-1.0	0.7	0.4
10	4 960.	-0.1	1.7	0.3
11	3 223.	-0.4	2.2	0.3
12	1 808.	-0.1	2.6	0.1
13	759.	-0.1	3.1	0.1
14	139.	-0.1	3.6	0.0

^a E_b (cm⁻¹) are the binding energies for the unperturbed potential. Δ (cm⁻¹) is the amount by which the vibrational levels are lowered. Case A (localized perturbation): $\Delta V = 5.5$ cm⁻¹ at $R = 3.25$ a.u. $\cong R_2(8)$, 0.01 cm⁻¹ $> \Delta V \rightarrow 0$ for $R \leq R_2(7) \cong 3.07$ a.u., and $R \geq R_2(9) \cong 3.48$ a.u.; Case B: $\Delta V = -4$ cm⁻¹ for $R \geq R_2(8)$, $\Delta V = 0$ for $R < R_2(8)$; Case C: $\Delta V = -4$ cm⁻¹ for $0 < R \leq 0.9$ a.u. $\cong R_1(4)$.

radial wavefunctions in a truncated harmonic-oscillator basis set and determine the coefficients variationally. Their results with basis sets of up to 100 terms were somewhat less accurate than the numerical (C-C) results [$T_0(v, 0)$ in error by up to ~ 6 cm^{-1}], as well as

being significantly slower. Greenawalt and Dickinson⁹ have extended their method using Morse-potential eigenfunctions as a basis set and achieved considerably greater success in terms of eigenvalue accuracy, with computation times comparable to the C-C method.

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Charge Transfer and Dissociative Charge Transfer between Rare-Gas Ions and Molecular Nitrogen*

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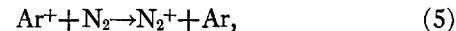
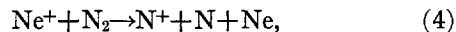
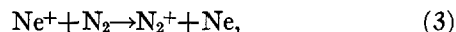
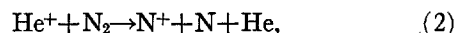
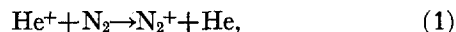
The reaction systems He^+ , Ne^+ , and $\text{Ar}^+ + \text{N}_2$ giving charge transfer and dissociative charge transfer have been studied for low collision energies. Kinetic-energy distributions and angular distributions of N_2^+ and N^+ have been measured. In all cases the reactions proceed via a variety of endothermic or exothermic channels. Product ions are found to be scattered at large c.m. scattering angles, but do not appear to be isotropic in the c.m. system. For dissociative charge transfer, the data are consistent with a two-step process involving first an electron transfer followed by predissociation. It is emphasized that these low-energy charge-transfer reactions are not conceptionally different from ion-molecule (reactive) collisions.

I. INTRODUCTION

During the past several years numerous charge-transfer and dissociative charge-transfer reactions between various atomic ions and molecules have been investigated which have large cross sections at very low collision energies.¹⁻⁵ Some exothermic reactions which exhibit this behavior have energy defects (ΔE) that are several electron volts, assuming ground-state reactants and products. In such highly exothermic reactions, the product ions are either produced in highly excited states or possess appreciable kinetic energy, depending upon how the excess energy is distributed among the translational and internal states of the products. Warneck² finds only indirect evidence for energetic products of several near-thermal-energy charge-transfer processes, and discusses the importance of energetic considerations in such reactions. Also, Moran and Friedman⁴ detected excess kinetic energy in the products of helium-ion-oxygen and helium-ion-nitrogen dissociative charge-transfer processes.

This paper reports the results of energetic and angular studies of the charge-transfer and dissociative charge-

transfer reactions



at low collision energies. The purpose of these studies was to obtain detailed information concerning the kinematics and dynamics of these reactions and ascertain, where possible, the final translational and internal states of the reaction products. Kinetic-energy distributions of the product ions of reactions (1)–(5) were measured for primary-beam laboratory energies over various intervals in the range 1.6–50 eV. Angular distributions of the product ions in Reactions (1)–(3) were also obtained at several collision energies in this range. The apparatus and the experimental procedure used in these investigations were the same as those employed in previous work performed in this laboratory⁶⁻⁸; both are described in detail in Ref. 6.

Briefly, the experimental method consists of directing a mass-analyzed and velocity-selected ion beam into a collision chamber containing target gas at low pressure. The product ions are velocity analyzed with a 127°

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