

Calculations of vibration-rotation energy levels of HD^+

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An artificial-channels scattering method [M. Shapiro and G. G. Balint-Kurti, *J. Chem. Phys.* **71**, 1461 (1979)] is used with a transformed Hamiltonian [R. E. Moss and I. A. Sadler, *Molec. Phys.* **66**, 591 (1989)] to calculate the energies of vibration-rotation levels for the ground electronic state of HD^+ . All nonadiabatic effects, except for part of the coupling of rotational and electronic angular momenta, are accounted for. The results, which are for $v=0-21$, $J=0,1$, together with some other levels involved in observed transitions, are compared with previous calculations, particularly those of Wolniewicz and Poll [*Molec. Phys.* **59**, 953 (1986)]. Inclusion of a correction to the energies of $J \neq 0$ levels to allow for the remaining contribution of Π electronic states permits comparison with experimental transition energies. The agreement is excellent.

I. INTRODUCTION

Vibration-rotation transition frequencies of HD^+ in its ground electronic state have been measured by Wing *et al.*¹ and Spezeski² for transitions involving low vibrational quantum numbers and by Carrington and colleagues³⁻⁹ for bands involving high v . The most extensive calculations so far are those of Wolniewicz and Poll,¹⁰ indeed, their theoretical values have been an invaluable guide for experiment. Other calculations should be mentioned: the variational calculations of Bishop and colleagues were restricted to $J=0$ and low v (0-2); the coupled-states calculations of Carrington and Kennedy⁵ and Kennedy *et al.*,¹³ the transformed Hamiltonian calculations of Moss and co-workers,¹³⁻¹⁵ and the hyperspheroidal coordinate calculations of Hara *et al.*¹⁶ did not include all the nonadiabatic corrections; the recent variational calculations of Moss and Sadler¹⁷ were limited to low v , although they extended to sufficiently high J that all the bound states for $v=0,1,2$ and some quasi-bound levels for $v=0,1$ were included.

In this paper a method of calculation is reported that makes use of the transformed Hamiltonian obtained by Moss and Sadler.¹⁵ This has the advantage that some of the interactions responsible for nonadiabatic effects, notably symmetry breaking, are removed from the kinetic-energy part of the Hamiltonian at the expense of the appearance of effective nuclear charges in the potential energy and of effective reduced masses. Of the remaining nonadiabatic terms, that responsible for the coupling of rotational and electronic angular momenta is neglected and it is the effect of $-(1/2\mu_{\text{eff}})(\partial^2/\partial R^2)$, where R is the internuclear separation, that is of particular interest here. The Hamiltonian used is described in Sec. II.

Section III is devoted to the description of the method

used to solve the Schrödinger equation with this transformed Hamiltonian. It is similar to that used in scattering problems with R playing the role of the scattering coordinate. To solve a bound-state problem using scattering-theory techniques, two *artificial* open channels are introduced in the manner used by Shapiro and Balint-Kurti^{18,19} for calculating the vibration-rotation energies of triatomic molecules. The artificial channels are coupled, in a well-specified asymmetric manner, to the bound states of interest but not to each other. The bound-state energies are found by monitoring the scattering-transition probability between the artificial open channels for different scattering energies, since at a bound-state energy the T -matrix element for transitions between the two open channels has a first-order pole. Shapiro and Balint-Kurti^{18,19} used the same basis functions at all values of the scattering coordinate but, since here very accurate results are required and high vibrational levels are considered, it is necessary to modify their method so that the basis functions may be changed as R changes.

Section IV presents the results obtained. For $J=0,1$ all vibrational levels ($v=0-21$) are included except for $v=22$. For $J > 1$ only those vibrational levels used for comparison with other calculations and those involved in spectroscopic transitions that have been observed are reported. For $J=0$ a comparison is possible with earlier work^{10-12,15} for low v . For $J \neq 0$ it is possible to compare with the low- v variational calculations of Moss and Sadler,¹⁵ but only if a correction is made here for part of the coupling of rotational and electronic angular momenta. However, for the bulk of our calculations, it is the work of Wolniewicz and Poll¹⁰ that is of particular interest. To compare with their work we must include relativistic and radiative corrections, as well as the correc-

tions for neglected rotational-electronic coupling. Our calculated transition frequencies are in excellent agreement with experiment and display some systematic differences from the work of Wolniewicz and Poll.

Section V includes a discussion of the limitations of the method used and the prospects for further work.

II. THE HAMILTONIAN

The Hamiltonian for the hydrogen molecular cation HD^+ may be written as^{5,20}

$$\mathcal{H} = \mathcal{H}_{\text{BO}} + (1/\mu)\mathcal{H}_{\text{ad}} + (1/\mu_a)\mathcal{H}_{gu} . \quad (1)$$

Here the overall translational motion has been removed and the geometric center of the nuclei coordinate system is used. In atomic units

$$\mathcal{H}_{\text{BO}} = -\frac{1}{2}\nabla_g^2 - (1/r_1) - (1/r_2) + (1/R) \quad (2)$$

and in the Born-Oppenheimer approximation the Schrödinger equation

$$\mathcal{H}_{\text{BO}}\psi(r;R) = E_{\text{BO}}(R)\psi(r;R) \quad (3)$$

may be solved exactly for each bond length. The electronic states may be classified Σ, Π, \dots , and also g or u . The ground Σ_g and the first excited Σ_u electronic states have the same dissociation limit in this approximation. The energy as a function of bond length may then be used as the potential that governs the vibrational-rotational motion.

In allowing for the breakdown of the Born-Oppenheimer approximation the molecular Hamiltonian may be averaged over the Born-Oppenheimer wave function to give the adiabatic potential

$$E_{\text{ad}}(R) = E_{\text{BO}}(R) + \langle \psi_{\text{BO}} | (1/\mu)\mathcal{H}_{\text{ad}} | \psi_{\text{BO}} \rangle , \quad (4)$$

where

$$(1/\mu)\mathcal{H}_{\text{ad}} = -(1/2\mu)\nabla_R^2 - (1/8\mu)\nabla_g^2 , \quad (5)$$

and

$$(1/\mu) = (1/m_1) + (1/m_2) , \quad (6)$$

with m_1 and m_2 the masses of nuclei 1 (H) and 2 (D) relative to the electron mass. However, the adiabatic corrections are diagonal in the electronic state and in this approximation the two lowest electronic states still have the same dissociation limit.

To obtain the different dissociation limits, corresponding to $\text{H}^+ + \text{D}(1s)$ and $\text{D}^+ + \text{H}(1s)$, mixing of the Σ_g ground state and the Σ_u first excited state must be allowed for. This symmetry breaking is caused by the third term in Eq. (1),

$$(1/\mu_a)\mathcal{H}_{gu} = -(1/2\mu_a)(\nabla_g \cdot \nabla_R) , \quad (7)$$

where

$$(1/\mu_a) = (1/m_1) - (1/m_2) . \quad (8)$$

However, although this coupling of the ground and first excited electronic states is the major nonadiabatic (off diagonal in the electronic state) effect, the contribution of

higher Σ states must be included in an accurate calculation. In addition, the coupling of rotational and electronic angular momentum, which mixes Σ and Π states for rotational quantum states that are associated with nonzero rotational quantum numbers J , should be included. (Although Σ, Π, \dots , and, in particular, g, u are no longer true symmetry labels, these symbols will be used as near-symmetry labels to refer to different electronic states.)

The symmetry-breaking part of the Hamiltonian (7) may be removed by subjecting the Hamiltonian to a unitary transformation.^{13,14} This is largely at the expense of introducing effective nuclear charges into the potential energy and effective reduced masses. All g/u mixing, that is, mixing caused by the term \mathcal{H}_{gu} [see Eq. (7)] in the Hamiltonian, which prevents the inversion operation i from being a true symmetry operation, is completely accounted for in the transformed potential-energy operator. However, mixing of Π_g states and excited Σ_g states with the ground Σ_g state is not allowed for.

Further transformation¹⁵ of the Hamiltonian removes cross derivatives between electronic and nuclear coordinates. The relationship of the final transformed Hamiltonian to that expressed in hyperspheroidal coordinates (see, for example, Ref. 16) is discussed in Ref. 15. If, as in this paper, rotational-electronic coupling is neglected, the ultimate transformed Hamiltonian for Σ states may be written in terms of (transformed) prolate spheroidal coordinates,

$$\xi = (r_1 + r_2)/R, \quad \infty > \xi \geq 1 \quad (9)$$

$$\eta = (r_1 - r_2)/R, \quad 1 \geq \eta \geq -1 \quad (10)$$

as

$$\begin{aligned} \mathcal{H}'' = & -(2\rho^2/mR^2)X_0 - (\rho/\mu_{\text{eff}}R^2)(2Y+3) + \rho^{1/2}V' \\ & - (1/2\mu_{\text{eff}})[(\partial^2/\partial R^2) + (5/R)(\partial/\partial R) \\ & + (3/R^2) - \rho J(J+1)/R^2] . \end{aligned} \quad (11)$$

Here

$$\begin{aligned} X_0 = & (\xi^2 - \eta^2)^{-1} [(\partial/\partial \xi)(\xi^2 - 1)(\partial/\partial \xi) \\ & + (\partial/\partial \eta)(1 - \eta^2)(\partial/\partial \eta)] , \end{aligned} \quad (12)$$

$$Y = (\xi^2 - \eta^2)^{-1} [\xi(\xi^2 - 1)(\partial/\partial \xi) + \eta(1 - \eta^2)(\partial/\partial \eta)] , \quad (13)$$

and

$$\rho = 1 + (m/4\mu_{\text{eff}})(\xi^2 + \eta^2 - 1) . \quad (14)$$

The two mass parameters in Eq. (11), μ_{eff} and m , may be expressed in terms of

$$p = [2 + (1/\mu)]\mu_a . \quad (15)$$

as

$$(1/\mu_{\text{eff}}) = (1/\mu_a)(p^2 - 1)^{1/2} - 2 \quad (16)$$

$$\approx (1/\mu) - (1/4\mu_a^2) + O(1/\mu\mu_a^2) \quad (17)$$

and

$$1/m = 1 + (1/4\mu_{\text{eff}}) . \quad (18)$$

The transformed potential energy is $\rho^{1/2}V'$, where

$$V' = -(2/R)[(Z_1 + Z_2)\xi + (Z_2 - Z_1)\eta](\xi^2 - \eta^2)^{-1} \\ + (1/R)[1 + \beta\xi\eta + \gamma(\xi^2 + \eta^2)]^{-1/2} , \quad (19)$$

with the effective nuclear charges

$$Z_1 = [(p-1)/(p+1)]^{1/4} \quad (20)$$

and

$$Z_2 = [(p+1)/(p-1)]^{1/4} , \quad (21)$$

and with

$$\beta = (p^2 - 1)^{-1/2} \approx (1/2\mu_a) + O(1/\mu_a, 1/\mu_a^2) \quad (22)$$

and

$$\gamma = (p\beta - 1)/2 \approx (1/16\mu_a^2) + O(1/\mu_a^2) . \quad (23)$$

In Eq. (11) nuclear-motion effects, apart from the nonadiabatic coupling due to the operators involving derivatives with respect to R , have now been brought within an adiabatic approximation. The Hamiltonian [Eq. (11)] also has the desirable properties that at dissociation the correct atomic limits are obtained and the electron density at the nucleus of the atom to which dissociation occurs is also correct.

The term in Eq. (11) involving the first derivative with respect to R may be removed by replacing the wave function ψ'' corresponding to \mathcal{H}'' by

$$\psi' = R^{-5/2} \psi_t . \quad (24)$$

At the same time the volume element is changed from

$$R^5 dR (\xi^2 - \eta^2) d\xi d\eta d\chi / 8$$

to

$$d\tau = dR (\xi^2 - \eta^2) d\xi d\eta d\chi / 8 . \quad (25)$$

The Hamiltonian appropriate to ψ_t is now

$$\mathcal{H}_t = -(1/2\mu_{\text{eff}})(\partial^2/\partial R^2) + \mathcal{H}_e , \quad (26)$$

where

$$\mathcal{H}_e = -(2\rho^2/mR^2)X_0 - (\rho/\mu_{\text{eff}}R^2)(2Y + 3) \\ + (\rho/\mu_{\text{eff}}R^2)J(J+1) + (3/8\mu_{\text{eff}}R^2) + \rho^{1/2}V' \quad (27)$$

does not contain any derivatives with respect to R , although it still contains R as a parameter. In the kinetic-energy operator only $-(1/2\mu_{\text{eff}})(\partial^2/\partial R^2)$ couples electronic states and it is the effect of the nonadiabatic coupling due to this operator that is the main interest in this paper.

In Ref. 15 the matrix elements of the Hamiltonian \mathcal{H}_e were found between the basis functions

$$\phi_i = (2\pi)^{-1/2} \exp[-\alpha(\xi-1)/2] L_{m_i}^{(0)}[\alpha(\xi-1)] P_{n_i}(\eta) , \quad (28)$$

where $P_{n_i}(\eta)$ and $L_{m_i}^{(0)}[\alpha(\xi-1)]$ are the Legendre and as-

sociated Laguerre polynomials, respectively. The term $\rho^{1/2}V'$ was expanded as a Taylor series and terms of order higher than $(1/\mu)^2$ and $(1/\mu_a)^2$ were neglected. The same basis functions and expansion are used here. The Schrödinger equation corresponding to the Hamiltonian \mathcal{H}_e is then solved variationally in this basis, for fixed values of R , and the nonlinear parameter α is optimized at a large number of R values (see Ref. 15).

In Sec. III matrix elements of the Hamiltonian, Eq. (27), between the basis functions, Eq. (28), are needed as well as the overlap matrix elements. The integrals required may be evaluated analytically as in Ref. 13. In addition, overlap matrix elements between basis functions with different values of the parameter α are needed, since different values of α are adopted for different ranges of R , but these integrals may also be evaluated analytically using the methods described in Ref. 17.

III. THE ARTIFICIAL-CHANNELS METHOD FOR THE CALCULATION OF BOUND-STATE EIGENVALUES

In the standard close-coupling method for solving time-independent quantum-mechanical inelastic scattering problems the full Hamiltonian for the problem is integrated between basis functions corresponding to the eigenfunctions of the separated fragments.²¹ This leaves a set of coupled second-order differential equations only in the scattering coordinate R . In the present work we take the matrix elements of the transformed Hamiltonian \mathcal{H}_t [Eq. (26)] between the basis functions [Eq. (28)] and obtain a similar set of coupled differential equations in R .

Shapiro²² has shown how the bound states of a Hamiltonian represented in this manner may be found using the standard techniques of inelastic quantum-mechanical scattering theory. The methods proposed in his paper have been applied to the calculations of bound-state energies for some molecular systems.^{18,19} In Shapiro's artificial-channels method two artificial scattering channels are added to the set of channels or basis functions representing the bound-state manifold. These artificial channels are open at asymptotically large R values, whereas the original bound-state channels are all closed (that is, they correspond to negative kinetic energies). The two artificial channels are coupled in a well-defined asymmetric manner to the bound-state channels, but are not coupled at all to each other. The solution of the scattering problem yields a transition or \underline{T} matrix between the open channels. The \underline{T} -matrix elements depend on the energy at which the scattering calculation is performed.

In the artificial-channels method the energy dependence of the \underline{T} -matrix element between the two artificial channels is computed. It has been shown,^{22,19} that the energy dependence of this matrix element possesses a first-order pole at the energy of each of the bound states. Because the analytic form of the energy dependence of the \underline{T} -matrix element is known, the exact values of the bound-state energies may be very efficiently located (see Appendix of Ref. 19). For each vibration-rotation level a trial energy is chosen and the open channels are defined

so that the scattering energy is small; in this way the scattering wave function has a long wavelength and the overlap with the bound-state wave function is good.

The coupled equations are solved by starting at small R and propagating the solution outwards using the log-derivative method.^{23,24} For the lowest vibrational state, $v=0$, only a small range of R values is important and only one set of basis functions (that is, one value of α) is needed. In addition, only a small number (35) of basis functions are necessary. However, for higher vibrational states a wide range of R values is sampled, the average bond length for $v=21$, $J=0$ being about $13a_0$. The use of one set of basis functions (that is, one value of α) for all the important values of R is not sufficient to ensure accurate results for the higher vibrational states. It is also found that, to attain the very high accuracies we are here aiming for, the number of basis functions must be considerably increased for the higher vibrational states. Rather than change α for every value of R , the range of R is divided into segments and within each segment the same α is used. In going from one segment to the next, as the wave function is propagated to higher R , it is necessary to match the wave functions at the boundary; this is done by using the overlap matrix. For $v=20$ as many as 90 basis functions and 54 segments, with α varying from 2.2 at $R=0.1a_0$ to 26.5 at $R=40a_0$, are used. Satisfactory results are also obtained for $v=21$, $J=0,1$ using 104 basis functions and 88 segments. Unfortunately the method is computer intensive and it has not proved possible to consider $v=21$, $J>1$ and the very highest levels, $v=22$, $J=0,1$; these lie within 8 cm^{-1} of the dissociation limit and, in the case of $v=22$, $J=1$, the average bond length is $41a_0$.

Using the results of Wolniewicz and Poll¹⁰ as a guide, good initial choices of the bound-state energies may be made and the convergence to the exact nonadiabatic energies is usually very rapid, rarely involving more than five iterations. The absolute energies of the bound states are thought to be accurate to better than $1 \times 10^{-9} E_h$

(0.0002 cm^{-1}). In calculating the energy relative to dissociation, the dissociation limit is taken to be $-0.499\,863\,815\,2E_h$ and the conversion to wave number units is $1 E_h = 219\,474.630\,67\text{ cm}^{-1}$ from the 1986 constants.²⁵ Unfortunately these calculations do not provide wave functions, and properties other than energies have not been calculated.

IV. RESULTS

In this section the results are presented in such a way as to facilitate comparison with previous calculations and with experiment.

A. Absolute nonadiabatic energies ($J=0$)

The few results available for comparison of absolute energies are for $J=0$ and low v . Those published before 1986 use different masses from those²⁵ employed in this paper, and are given in the first half of Table I together with the results of our calculations using the same masses as the original investigators. The disagreement with Bishop and Cheung¹¹ becomes greater with increasing v , although our value for the (0,0) level agrees exactly with the later calculation of Bishop and Solunac.¹² In addition, no explanation may be offered for the disagreement with the (0,0) value of Wolniewicz and Poll,¹⁰ since our calculations give the same result whether their masses or the masses of Bishop^{11,12} are used.

It was possible to make similar remarks in Ref. 17, where the variational results of Moss and Sadler were compared with those in Refs. 10–12. The reason for this becomes clear from the second half of Table I, where the results of the present calculations are compared with those for the variational calculations of Ref. 17. The agreement is excellent and it is thought that the small discrepancies for $v=3$ and 4 are just a reflection of the fact that the variational calculations did not converge satisfactorily for higher v .

TABLE I. Nonadiabatic energies for the $J=0$ vibration-rotation levels of the ground electronic state of HD^+ together with a comparison with other calculations; relativistic and radiative corrections are *not* included. A supposed misprint in Ref. 10 has been corrected. The masses are relative to that of the electron.

Level (v, J)	Masses		Energy (E_h)	
	m_H	m_D	Other work	This work
(0,0)	1836.152 746	3670.479 071	-0.597 897 9674 ^a	-0.597 897 9678
(1,0)			-0.589 181 8255 ^a	-0.589 181 8274
(2,0)			-0.580 903 6794 ^a	-0.580 903 6969
(0,0)			-0.597 897 967 80 ^b	-0.597 897 9678
(0,0)	1836.1528	3670.4786	-0.597 897 9726 ^c	-0.597 897 9677
(0,0)	1836.152 701	3670.483 014	-0.597 897 9686 ^d	-0.597 897 9686
(1,0)			-0.589 181 8297 ^d	-0.589 181 8297
(2,0)			-0.580 903 7004 ^d	-0.580 903 7004
(3,0)			-0.573 050 5467 ^d	-0.573 050 5469
(4,0)			-0.565 611 0422 ^d	-0.565 611 0424

^aReference 11.

^bReference 12.

^cReference 10.

^dReference 17.

B. Nonadiabatic dissociation energies for $J > 0$

For nonzero J all previously published results have included relativistic and radiative corrections, except for those of Ref. 17. However, the latter may not be compared directly with the present work since here the rotational-electronic coupling term in the transformed Hamiltonian is neglected. This means that no account has been taken of the mixing of Π_g states into the electronic ground state. Nevertheless, the appropriate corrections are tabulated in Table III of Ref. 10 for $J = 1, 3, \text{ and } 5$, and extrapolation to $J = 8$ is thought¹⁰ to be justified. In Ref. 17 excellent agreement was found with these Π_g contributions¹⁰ and so they are used here and in the remainder of the paper; the effect on these corrections of the difference in the masses used in the various calculations is negligible.

In Table II, then, the appropriate comparison is given. Again the agreement is excellent, although for $v = 3$ it is slightly poorer, as might be expected. The comparisons presented in Tables I and II give us confidence in both the present work and the variational calculations.¹⁷

C. Dissociation energies including relativistic and radiative corrections

Table III contains the bulk of the results of this paper, namely, the nonadiabatic dissociation energies of $v = 0-21$ for $J = 0, 1$ and of selected v for $J > 1$. To these may be added the Π_g contributions,¹⁰ but for comparison with the results of Wolniewicz and Poll¹⁰ it is also necessary to add both relativistic and radiative corrections, since they do not quote these or the uncorrected dissociation energies. As in Ref. 17 the relativistic corrections are obtained as a function of R using the results of Bishop²⁶ as modified by Gonsalves and Moss,²⁷ while the

radiative corrections are taken from Bishop and Cheung,²⁸ but with the Bethe logarithm chosen to be 2.29 so that the atomic limit is given at large bond lengths. The corrections for each vibration-rotation level are then obtained as differences between energies calculated (using the Numerov-Cooley algorithm²⁹) for an adiabatic potential both with and without the relevant correction. The relativistic corrections given in Table III agree to 0.001 cm^{-1} , with the more sophisticated calculations of Kennedy and Howells.³⁰ The least secure part of the calculations is for the radiative corrections, but only the differences in these are needed when experiment is compared with theory in Sec. IV D.

The final column in Table III gives the differences between our results and those of Wolniewicz and Poll.¹⁰ In general the agreement is good for low v and high v , but for intermediate v the discrepancies are significant. Indeed, the differences are seen to follow a systematic behavior and are greatest for those v values for which the nonadiabatic corrections due to mixing in of Σ_g states are expected to be largest. No explanation can be offered for the lack of agreement; sample calculations show that the use of different masses makes at most 0.002 cm^{-1} difference and using the dissociation energy or conversion factor from E_h to cm^{-1} in Ref. 10 has even less effect.

D. Transition energies

All the available experimental data are given in Table IV, except for transitions involving $v = 21, J = 2, 3$ (Ref. 6) and $v = 22, J = 0, 1$ (Refs. 8 and 9). As expected from the accord of the present calculations with the variational calculations of Ref. 17 the agreement of theory with experiment for low v is excellent. The agreement with the data of Carrington and colleagues³⁻⁶ for transitions involving levels with high v is also splendid, with the ma-

TABLE II. Comparison of the dissociation energies of selected vibration-rotation levels of the ground electronic state of HD^+ calculated in this paper with the variational calculations of Moss and Sadler (Ref. 17). Relativistic and radiative corrections are *not* included. Corrections for Σ_g - Π_g mixing induced by rotational-electronic angular momentum coupling are taken from Ref. 10.

(v, J)	Uncorrected dissociation energy (cm^{-1})	Π_g correction ^a (cm^{-1})	Dissociation energy (cm^{-1})	
			This work	Ref. 17
(0,1)	21 472.1483	0.0014	21 472.1497	21 472.1497
(0,3)	21 254.1493	0.0083	21 254.1576	21 254.1575
(0,5)	20 867.1365	0.0204	20 867.1569	20 867.1571
(1,1)	19 561.1792	0.0014	19 561.1806	19 561.1806
(1,3)	19 353.1439	0.0081	19 353.1520	19 353.1520
(1,5)	18 983.8693	0.0201	18 983.8894	18 983.8894
(2,1)	17 746.2812	0.0013	17 746.2825	17 746.2825
(2,3)	17 547.9078	0.0080	17 547.9158	17 547.9156
(2,5)	17 195.8378	0.0198	17 195.8576	17 195.8575
(3,1)	16 024.6014	0.0013	16 024.6027	16 024.6024
(3,3)	15 835.6253	0.0078	15 835.6331	15 835.6327

^aReference 10.

^bReference 17.

TABLE III. Dissociation energies in cm^{-1} for vibration-rotation levels of the ground electronic state of HD^+ , including relativistic and radiative corrections, together with a comparison with the values of Wolniewicz and Poll (Ref. 10) (the differences are given to three decimal places).

(v, J)	Uncorrected dissociation energy	Π_g^a	Corrections		Dissociation energy	Difference between values of Ref. 10 and this work
			Relativistic	Radiative		
(0,0)	21 516.0096		0.1407	-0.0812	21 516.0691	0.002
(1,0)	19 603.0382		0.1087	-0.0732	19 603.0737	0.004
(2,0)	17 786.1989		0.0796	-0.0657	17 786.2128	0.005
(3,0)	16 062.6309		0.0532	-0.0587	16 062.6254	0.007
(4,0)	14 429.8484		0.0293	-0.0522	14 429.8255	0.008
(5,0)	12 885.7300		0.0079	-0.0461	12 885.6918	0.010
(6,0)	11 428.5124		-0.0109	-0.0405	11 428.4610	0.010
(7,0)	10 056.7886		-0.0272	-0.0352	10 056.7262	0.011
(8,0)	8 769.5098		-0.0412	-0.0304	8 769.4382	0.012
(9,0)	7 565.9926		-0.0529	-0.0258	7 565.9139	0.013
(10,0)	6 445.9306		-0.0623	-0.0217	6 445.8466	0.014
(11,0)	5 409.4124		-0.0695	-0.0180	5 409.3249	0.015
(12,0)	4 456.9446		-0.0744	-0.0146	4 456.8556	0.014
(13,0)	3 589.4847		-0.0768	-0.0115	3 589.3964	0.015
(14,0)	2 808.4802		-0.0770	-0.0088	2 808.3944	0.014
(15,0)	2 115.9191		-0.0745	-0.0064	2 115.8382	0.013
(16,0)	1 514.3886		-0.0696	-0.0044	1 514.3146	0.012
(17,0)	1 007.1436		-0.0621	-0.0027	1 007.0788	0.010
(18,0)	598.1587		-0.0520	-0.0015	598.1052	0.010
(19,0)	292.1173		-0.0391	-0.0005	292.0777	0.006
(20,0)	94.0754		-0.0233	0.0000	94.0521	0.003
(21,0)	10.2140		-0.0045	0.0000	10.2095	0.000
(0,1)	21 472.1483	0.0014	0.1390	-0.0809	21 472.2078	0.001
(1,1)	19 561.1792	0.0014	0.1072	-0.0730	19 561.2148	0.004
(2,1)	17 746.2812	0.0013	0.0782	-0.0655	17 746.2952	0.005
(3,1)	16 024.6014	0.0013	0.0519	-0.0584	16 024.5962	0.006
(4,1)	14 393.6611	0.0013	0.0281	-0.0519	14 393.6386	0.008
(5,1)	12 851.3464	0.0013	0.0068	-0.0458	12 851.3087	0.009
(6,1)	11 395.9014	0.0012	-0.0119	-0.0402	11 395.8505	0.009
(7,1)	10 025.9266	0.0012	-0.0282	-0.0350	10 025.8646	0.010
(8,1)	8 740.3812	0.0012	-0.0421	-0.0302	8 740.3101	0.012
(9,1)	7 538.5897	0.0012	-0.0537	-0.0257	7 538.5115	0.013
(10,1)	6 420.2547	0.0011	-0.0630	-0.0215	6 420.1713	0.014
(11,1)	5 385.4743	0.0011	-0.0702	-0.0179	5 385.3873	0.015
(12,1)	4 434.7660	0.0011	-0.0749	-0.0145	4 434.6777	0.014
(13,1)	3 569.0995	0.0011	-0.0773	-0.0114	3 569.0119	0.014
(14,1)	2 789.9365	0.0010	-0.0774	-0.0087	2 789.8514	0.014
(15,1)	2 099.2818	0.0010	-0.0749	-0.0064	2 099.2015	0.012
(16,1)	1 499.7442	0.0009	-0.0699	-0.0044	1 499.6708	0.012
(17,1)	994.6048	0.0008	-0.0622	-0.0026	994.5408	0.010
(18,1)	587.8761	0.0008	-0.0519	-0.0014	587.8236	0.009
(19,1)	284.2921	0.0007	-0.0389	-0.0004	284.2535	0.005
(20,1)	88.9982	0.0005	-0.0229	0.0000	88.9758	0.002
(21,1)	8.5495	0.0000	-0.0040	0.0000	8.5455	0.007
(0,2)	21 384.6882	0.0041	0.1358	-0.0803	21 384.7478	0.001
(1,2)	19 477.7141	0.0040	0.1041	-0.0724	19 477.7498	0.003
(2,2)	17 666.6898	0.0040	0.0754	-0.0648	17 666.7044	0.005
(3,2)	15 948.7775	0.0039	0.0493	-0.0579	15 948.7728	0.005
(14,2)	2 753.0229	0.0030	-0.0781	-0.0085	2 752.9393	0.014
(15,2)	2 066.1804	0.0029	-0.0754	-0.0062	2 066.1017	0.012
(16,2)	1 470.6294	0.0027	-0.0701	-0.0042	1 470.5578	0.011
(17,2)	969.7062	0.0025	-0.0624	-0.0026	969.6437	0.009
(18,2)	567.4983	0.0023	-0.0519	-0.0013	567.4474	0.008

TABLE III. (Continued).

(v, J)	Uncorrected dissociation energy	Π_g^a	Corrections		Dissociation energy	Difference between values of Ref. 10 and this work
			Relativistic	Radiative		
(20,2)	79.0841	0.0015	-0.0223	0.0000	79.0633	0.002
(0,3)	21 254.1493	0.0083	0.1311	-0.0794	21 254.2093	0.000
(1,3)	19 353.1439	0.0081	0.0997	-0.0715	19 353.1802	0.003
(2,3)	17 547.9078	0.0080	0.0712	-0.0641	17 547.9229	0.003
(3,3)	15 835.6253	0.0078	0.0454	-0.0571	15 835.6214	0.005
(14,3)	2698.0839	0.0060	-0.0791	-0.0082	2698.0026	0.013
(15,3)	2016.9579	0.0058	-0.0762	-0.0059	2016.8816	0.012
(16,3)	1427.3896	0.0054	-0.0707	-0.0040	1427.3203	0.012
(17,3)	932.8002	0.0050	-0.0625	-0.0023	932.7404	0.010
(18,3)	537.3933	0.0045	-0.0516	-0.0010	537.3452	0.007
(20,3)	64.8274	0.0029	-0.0211	0.0000	64.8092	-0.001
(14,4)	2625.6298	0.0100	-0.0805	-0.0077	2625.5516	0.012
(16,4)	1370.5384	0.0090	-0.0713	-0.0036	1370.4725	0.010
(17,4)	884.4144	0.0083	-0.0627	-0.0021	884.3579	0.009
(18,4)	498.1184	0.0074	-0.0513	-0.0008	498.0737	0.006
(20,4)	47.0040	0.0046	-0.0195	0.0000	46.9891	-0.006
(0,5)	20 867.1365	0.0204	0.1171	-0.0767	20 867.1973	-0.002
(1,5)	18 983.8693	0.0201	0.0867	-0.0689	18 983.9072	0.001
(2,5)	17 195.8378	0.0198	0.0590	-0.0616	17 195.8550	0.002
(14,5)	2536.3285	0.0150	-0.0822	-0.0072	2536.2541	0.013
(15,5)	1872.3437	0.0142	-0.0783	-0.0050	1872.2746	0.011
(16,5)	1300.7514	0.0134	-0.0719	-0.0032	1300.6897	0.011
(17,5)	825.2455	0.0123	-0.0628	-0.0018	825.1932	0.009
(18,5)	450.4137	0.0110	-0.0508	-0.0006	450.3733	0.006
(15,6)	1778.4377	0.0198	-0.0796	-0.0044	1778.3735	0.012
(16,6)	1218.8600	0.0186	-0.0726	-0.0027	1218.8033	0.012
(17,6)	756.1564	0.0171	-0.0627	-0.0013	756.1095	0.008
(18,6)	395.2060	0.0151	-0.0501	-0.0003	395.1707	0.005
(15,7)	1671.3648	0.0262	-0.0809	-0.0039	1671.3062	0.014
(18,7)	333.6150	0.0198	-0.0489	0.0000	333.5859	0.005
(17,8)	592.4871	0.0284	-0.0621	-0.0004	592.4530	0.011

^aReference 10.

majority of the calculated values agreeing with experiment to 0.001 cm^{-1} , which is the experimental error.

These results are a significant improvement on those of Wolniewicz and Poll.¹⁰ Broadly speaking, the discrepancies between their calculated values and experiment reflect the differences between our results and theirs for the dissociation energies given in Table III. This suggests that our results in Table III are to be preferred.

V. DISCUSSION

This paper presents calculated dissociation energies for many vibration-rotation levels of the ground electronic state of HD^+ . Unlike Ref. 17, which concentrated on high J , results are reported for high as well as low v . However, for $J > 0$ it is necessary to use the published¹⁰

corrections for the effect of rotationally induced $\Sigma_g - \Pi_g$ mixing. Agreement with experiment is excellent, but as the experiments yield only energy differences, there could still be significant errors in the nonadiabatic, relativistic, or radiative corrections. Our comparison with experiment only provides support for the accuracy of calculated differences in these corrections between vibration-rotation levels. The radiative corrections are thought to be the weakest part of the calculation. Nevertheless, we are confident that the energy of any transition involving $v < 21$ and $J < 9$ could be predicted to 0.001 cm^{-1} . The only reason that all these vibration-rotation energies have not been calculated is that a separate calculation is needed for each.

The same method may be applied to H_2^+ and D_2^+ , although in these cases symmetry breaking does not occur

and i is a true symmetry operation, unless account is taken of nuclear spin. In addition, vibration-rotation levels of the shallow potential minima associated with the first excited electronic states are experimentally accessible.³¹ However, these levels have large average bond lengths and, like the $v=21, J=2,3$ and $v=22, J=0,1$ levels of the ground electronic state of HD^+ , it may be that the

calculations will not be computationally feasible. At present our computer program spends about 95% of its running time inverting matrices, which is very time consuming.

A more demanding problem than HD^+ is $(d\text{t}\mu)^+$, for which the breakdown of the Born-Oppenheimer approximation is much more serious, since the muon has a mass

TABLE IV. Comparison of calculated and experimental transition frequencies in cm^{-1} for the ground electronic state of HD^+ .

Transition	Experiment	Theory		Difference between experiment and calculated values	
		This work	Ref. 10	This Work	Ref. 10
(1,0)-(0,1)	1869.134 ^a	1869.1341	1869.131	0.000	0.003
(1,1)-(0,2)	1823.533 ^a	1823.5330	1823.530	0.000	0.003
(1,2)-(0,3)	1776.459 ^b	1776.4595	1776.456	-0.001	0.003
(2,1)-(1,0)	1856.778 ^a	1856.7785	1856.778	-0.001	0.000
(3,1)-(2,0)	1761.616 ^a	1761.6166	1761.616	-0.001	0.000
(3,2)-(2,1)	1797.522 ^a	1797.5224	1797.522	0.000	0.000
(3,3)-(2,2)	1831.083 ^b	1831.0830	1831.083	0.000	0.000
(3,1)-(2,2)	1642.108 ^a	1642.1082	1642.107	0.000	0.001
(17,1)-(14,0)	1813.852 ^c	1813.8536	1813.857	-0.002	-0.005
(17,2)-(14,1)	1820.209 ^c	1820.2077	1820.212	0.001	-0.003
(17,3)-(14,2)	1820.200 ^c	1820.1989	1820.203	0.001	-0.003
(17,4)-(14,3)	1813.645 ^c	1813.6447	1813.649	0.000	-0.004
(17,5)-(14,4)	1800.358 ^c	1800.3584	1800.362	0.000	-0.004
(17,6)-(14,5)	1780.145 ^c	1780.1446	1780.149	0.000	-0.004
(17,0)-(14,1)	1782.772 ^c	1782.7726	1782.776	-0.001	-0.004
(18,1)-(16,0)	926.4895 ^d	926.4910	926.494	-0.002	-0.004
(18,2)-(16,1)	932.2237 ^d	932.2234	932.228	0.000	-0.004
(18,3)-(16,2)	933.2129 ^d	933.2126	933.217	0.000	-0.004
(18,4)-(16,3)	929.2471 ^d	929.2466	929.252	0.001	-0.005
(18,5)-(16,4)	920.1001 ^d	920.0992	920.104	0.001	-0.004
(18,6)-(16,5)	905.5191 ^d	905.5190	905.525	0.000	-0.006
(18,7)-(16,6)	885.2183 ^d	885.2174	885.224	0.001	-0.006
(18,0)-(16,1)	901.5648 ^d	901.5656	901.568	-0.001	-0.003
(18,1)-(16,2)	882.7312 ^d	882.7342	882.736	-0.003	-0.005
(17,0)-(15,1)	1092.124 ^e	1092.1227	1092.125	0.001	-0.001
(17,1)-(15,2)	1071.561 ^e	1071.5609	1071.563	0.000	-0.002
(17,2)-(15,3)	1047.239 ^e	1047.2379	1047.241	0.001	-0.002
(17,4)-(15,5)	987.917 ^e	987.9167	987.919	0.000	-0.002
(17,5)-(15,6)	953.180 ^e	953.1803	953.184	0.000	-0.004
(17,8)-(15,7)	1078.8532 ^d	1078.8532	1078.856	0.000	-0.003
(20,0)-(17,1)	900.488 ^e	900.4887	900.496	-0.001	-0.008
(20,1)-(17,2)	880.668 ^e	880.6679	880.675	0.000	-0.007
(20,1)-(17,0)	918.102 ^e	918.1030	918.111	-0.001	-0.009
(20,2)-(17,1)	915.476 ^e	915.4775	915.486	-0.002	-0.010
(20,3)-(17,2)	904.833 ^e	904.8345	904.845	-0.002	-0.012
(20,4)-(17,3)	885.749 ^e	885.7513	885.767	-0.002	-0.018
(21,0)-(17,1)	984.330 ^f	984.3313	984.341	-0.001	-0.011
(21,1)-(17,0)	998.533 ^f	998.5333	998.536	0.000	-0.003

^aReference 1.

^bReference 2.

^cReference 4.

^dReference 3.

^eReference 5.

^fReference 6.

207 times that of the electron. Our present program is not expected to rival the results of other workers (see, for example, Ref. 32), unless we avoid the approximation of retaining only the first few terms in the Taylor expansion of $\rho^{1/2}V'$ in the transformed Hamiltonian, Eq. (27).

An obvious extension of this work would be to include Π functions in the electronic basis used, as in the variational calculations of Moss and Sadler.¹⁷ This would remove our reliance on the corrections of Wolniewicz and Poll¹⁰ for part of the coupling of rotational and electronic angular momentum. In addition, it might make accessi-

ble high- v , high- J levels, which are of current experimental interest.⁷

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- ¹W. H. Wing, G. A. Ruff, W. E. Lamb, and J. J. Spezeski, *Phys. Rev. Lett.* **36**, 1488 (1976).
- ²J. J. Spezeski, Ph.D. thesis, Yale University, 1977.
- ³A. Carrington, J. Buttenshaw, and P. G. Roberts, *Mol. Phys.* **38**, 1711 (1979); A. Carrington and J. Buttenshaw, *Mol. Phys.* **44**, 267 (1981).
- ⁴A. Carrington, J. Buttenshaw, and R. A. Kennedy, *Mol. Phys.* **48**, 775 (1983).
- ⁵A. Carrington and R. A. Kennedy, *Mol. Phys.* **56**, 935 (1985).
- ⁶A. Carrington, I. R. McNab, and C. A. Montgomerie, *J. Chem. Phys.* **87**, 3246 (1987); *Mol. Phys.* **64**, 983 (1988).
- ⁷A. Carrington, I. R. McNab, and C. A. Montgomerie, *Chem. Phys. Lett.* **149**, 326 (1988).
- ⁸A. Carrington, I. R. McNab, and C. A. Montgomerie, *Mol. Phys.* **65**, 751 (1988).
- ⁹A. Carrington, I. R. McNab, C. A. Montgomerie, and J. M. Brown, *Mol. Phys.* **66**, 1279 (1989).
- ¹⁰L. Wolniewicz and J. D. Poll, *Mol. Phys.* **59**, 953 (1986).
- ¹¹D. M. Bishop and L. M. Cheung, *Phys. Rev. A* **16**, 640 (1977).
- ¹²D. M. Bishop and S. A. Solunac, *Phys. Rev. Lett.* **55**, 1986 (1985).
- ¹³R. A. Kennedy, R. E. Moss, and I. A. Sadler, *Mol. Phys.* **64**, 177 (1988).
- ¹⁴R. E. Moss and I. A. Sadler, *Chem. Phys. Lett.* **132**, 190 (1986); *Mol. Phys.* **61**, 905 (1987); **64**, 165 (1988).
- ¹⁵R. E. Moss and I. A. Sadler, *Mol. Phys.* **66**, 591 (1989).
- ¹⁶S. Hara, H. Fukuda, and T. Ishihara, *Phys. Rev. A* **39**, 35 (1989).
- ¹⁷R. E. Moss and I. A. Sadler, *Mol. Phys.* **68**, 1015 (1989).
- ¹⁸M. Shapiro and G. G. Balint-Kurti, *Faraday Discuss. Chem. Soc.* **62**, 51 (1977); I. F. Kidd, G. G. Balint-Kurti, and M. Shapiro, *ibid.* **71**, 287 (1981).
- ¹⁹M. Shapiro, and G. G. Balint-Kurti, *J. Chem. Phys.* **71**, 1461 (1979).
- ²⁰A. Carrington and R. A. Kennedy, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1984), Vol. 3, p. 393.
- ²¹G. G. Balint-Kurti, in *International Review of Science*, edited by A. D. Buckingham and C. A. Coulson (Butterworths, London, 1975), Ser. II, Vol. 1.
- ²²M. Shapiro, *J. Chem. Phys.* **56**, 2582 (1972).
- ²³B. R. Johnson, *J. Comp. Phys.* **13**, 445 (1973).
- ²⁴B. R. Johnson, in Lawrence Berkeley Laboratory Report No. LBL-9051, 1979 (unpublished).
- ²⁵E. R. Cohen and B. N. Taylor, *Rev. Mod. Phys.* **59**, 1121 (1987).
- ²⁶D. M. Bishop, *J. Chem. Phys.* **66**, 3842 (1977).
- ²⁷J. W. Gonsalves and R. E. Moss, *Chem. Phys. Lett.* **62**, 534 (1979).
- ²⁸D. M. Bishop and L. M. Cheung, *J. Chem. Phys.* **75**, 3155 (1981).
- ²⁹R. J. LeRoy, University of Waterloo Chemical Physics Research Report No. CP110, 1978 (unpublished).
- ³⁰R. A. Kennedy and M. H. Howells (unpublished).
- ³¹A. Carrington, I. R. McNab, and C. A. Montgomerie, *Phys. Rev. Lett.* **61**, 1573 (1988); *Chem. Phys. Lett.* **160**, 237 (1989); A. Carrington, I. R. McNab, C. A. Montgomerie, and R. A. Kennedy, *Mol. Phys.* **67**, 711 (1989).
- ³²S. A. Alexander and H. J. Monkhorst, *Phys. Rev. A* **38**, 26 (1988).