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Photodissociation of H_2^+ and D_2^+ : Theory*

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Theory is described and calculations made for photodissociation cross sections of H_2^+ (D_2^+) from each of the ion's 19 (27) vibrational levels. Cross sections are summed over an assumed Franck-Condon distribution of initial vibrational states to give a predicted cross section for comparison with experiment. Auxiliary calculations are made of some of the cross sections using the common δ -function approximation to the continuum radial wave functions, and a comparison made with the results using more exact wave functions shows very good agreement for photodissociation from the lowest vibrational levels, but very poor agreement for photodissociation from higher levels.

I. INTRODUCTION

For forty years or more physicists have been involved in calculating basic properties¹ of the simplest of all molecules, H_2^+ . Similarly, photodissociation of molecules² has long been a subject of inquiry. However, interest in both subjects is far from exhausted, and it is only in recent years that photodissociation of H_2^+ has received attention. The H_2^+ molecule is one of the few molecules where *ab initio* calculations can presently be made.

In 1952, Bates³ used a semiclassical method to calculate total absorption of radiation by H_2^+ at various temperatures. This was followed shortly by a quantum treatment by Buckingham *et al.*⁴ who calculated essentially the same quantities. These authors noted the possible astrophysical importance of this absorption. In 1956, Gibson⁵ and Linlor⁶ suggested photodissociation as a tool for trapping energetic particles in a magnetic mirror with hope of obtaining dense high-energy plasmas for controlled thermonuclear fusion. Gibson⁵ made a rough quantum calculation of the cross section for photodissociation of H_2^+ . Linlor *et al.*⁷ observed photodissociation of H_2^+ when a beam of the ions passed through the light from a mercury arc, and they made an order-of-magnitude estimate of the average cross section from the observations. Photodissociation of H_2^+ has since⁸⁻¹⁰ been used as a means of obtaining aligned samples of H_2^+ ions.

In 1963, Dunn¹¹ reported measurements of the cross section which were in gross disagreement with the theory of Gibson. This prompted new theoretical calculations which were reported¹² in 1965. Since agreement between theory and experiment was still poor, a new experiment was undertaken.¹³ The present paper reports in more detail the calculations and results reported briefly before¹² to give a basis for detailed analysis of the new experiment as well as a basis for using photodissociation as a diagnostic tool for vibrational-state populations as discussed in Sec. III. Recently an additional calculation has appeared,¹⁴ with which comparison will be made.

Calculations of photodissociation cross sections are outlined for both H_2^+ and D_2^+ from all 19 vibrational levels of H_2^+ and 27 levels of D_2^+ . The calculations make use of the accurate data available on potential functions¹⁵ and oscillator strengths;¹⁶ so that the limits of accuracy are set only by the limits of the Born-Oppenheimer separation of electronic and nuclear motions, the limits imposed by ignoring dynamic correction terms,¹⁷ and other minor approximations described.

A comparison of cross sections calculated using numerically generated continuum radial wave functions is made with those using the commonly applied δ -function approximation¹⁸ for these wave functions.

Individual cross sections are summed with appropriate weighting factors to give a predicted

cross section for comparison with the experiment.¹³

The large bulk of the results from the calculations (27 cross-section curves for D_2^+ and 19 cross-section curves for H_2^+) makes it impractical to communicate all the results here. Consequently, only representative results are reported, although all the results are available¹⁹ in detail in unpublished form.

II. CALCULATION

A. General

Relevant potential curves for H_2^+ are shown in Fig. 1. Transitions considered are from given vibrational levels of H_2^+ (D_2^+) in the $1s\sigma_g$ electronic state to various parts of the vibrational continuum of the $2p\sigma_u$ state. The $1s\sigma_g \rightarrow 2p\sigma_u$ transition is dipole-allowed, and is a parallel transition of the charge-transfer type.²⁰

The theory involved in the calculation is straightforward and may be summarized in the following steps:

1. Start with the transition probability per unit time,

$$w = (2\pi/\hbar)\rho(\epsilon)|H|^2 \quad (1)$$

2. Make the dipole approximation.
3. Use box normalization.
4. Divide by flux to get the differential cross section, and integrate over solid angle to get the total cross section.
5. Assume separability of electronic and nuclear motions (Born-Oppenheimer approximation).
6. Sum over magnetic substates.

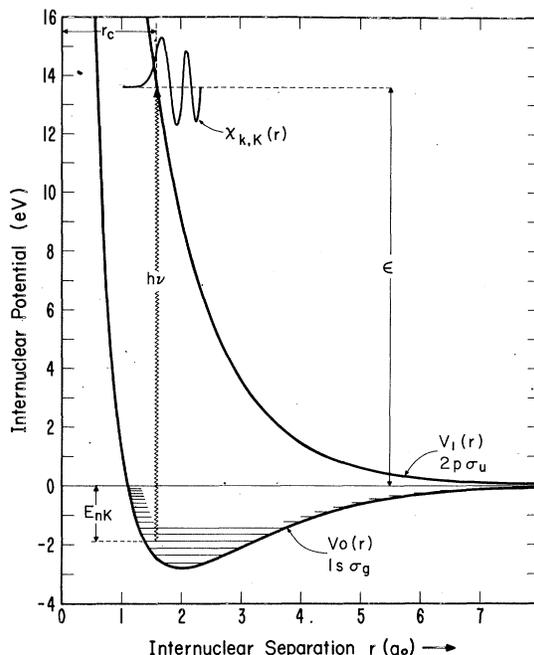


FIG. 1. Potential curves for the $1s\sigma_g$ and $2p\sigma_u$ states of H_2^+ taken from Ref. 15. A transition of the type considered in this paper is indicated by the jagged line. Also shown are continuum energy ϵ , classical turning radius r_c , vibration binding energy E_{nK} , and a typical continuum wave function $\chi_{kK}(r)$.

7. Average over molecule-polarization orientations.

Beyond these steps, the chore is essentially numerical and may be done with a computer.

B. Detail

The final density of states $\rho(\epsilon)$ appearing in Eq. (1) is, in this case, given by

$$\rho(\epsilon) = (L^3 \mu p / h^3) d\Omega, \quad (2)$$

where L^3 is a normalization volume, μ and p are the reduced mass and momentum, respectively, of the dissociating particles, and $d\Omega$ is an element of solid angle. Heitler²¹ gives the appropriate matrix element H , as well as the dipole approximation²² to H which we use here. By making these substitutions in Eq. (1) and dividing by the flux c/L^3 , we obtain an expression for the differential cross section

$$d\sigma = (\mu^2 \nu \nu / \hbar^3 c) |e \int \Psi_f^* \vec{\eta} \cdot \vec{z} \Psi_i d\vec{r}|^2 d\Omega. \quad (3)$$

Here ν is the frequency of incident light, e the electronic charge, $\vec{\eta}$ the polarization vector, and Ψ_i and Ψ_f the initial and final wave functions, respectively. The normalization volume no longer appears, provided the vector potential (in the original form²¹ of H) and Ψ_f are normalized in the same box.

We assume the usual separability of the wave functions (Born-Oppenheimer), so that the molecular wave functions can be expressed as a product of electronic (ψ) and nuclear (ξ) wave functions:

$$\Psi = \psi \xi. \quad (4)$$

In the bound $1s\sigma_g$ state,

$$\xi_i = Y_{KM}(\Theta, \Phi) R_{nK}(r), \quad (5)$$

where $Y_{KM}(\Theta, \Phi)$ are ordinary normalized spherical harmonics with angles defined in Fig. 2. The function $R_{nK}(r)$ satisfies the equation

$$[(d^2/dr^2) - \mu(E_{nK} + V_o(r)) - K(K+1)/r^2]rR_{nK}(r) = 0, \quad (6)$$

where $R_{nK}(r)$ is normalized so that

$$\int_0^\infty R_{nK}^2(r)r^2dr = \int_0^\infty \chi_{nK}^2(r)dr = 1. \quad (7)$$

Here r is internuclear separation, $V_o(r)$ the internuclear potential of the $1s\sigma_g$ state, and E_{nK} the energy eigenvalue of the state with vibrational quantum number n and rotational quantum number K .

In the repulsive $2p\sigma_u$ state, the proper boundary conditions for scattering must be satisfied, and the wave function may^{23,24} be expressed,

$$\xi_F = \sum_{K'} (2K'+1)(-i)^{K'} e^{i\delta_{K'}} P_{K'}(\cos \theta) R_{kK'}(r), \quad (8)$$

where $R_{kK'}(r)$ satisfies the equation

$$[(d^2/dr^2) + k^2 - \mu V_1(r) - K'(K'+1)/r^2]rR_{kK'}(r) = 0 \quad (9)$$

and has the form at large r given by

$$\chi_{kK'}(r) = rR_{kK'}(r) - (1/k)\sin[kr - \frac{1}{2}(K'+\frac{1}{2})\pi + \delta_{K'}]. \quad (10)$$

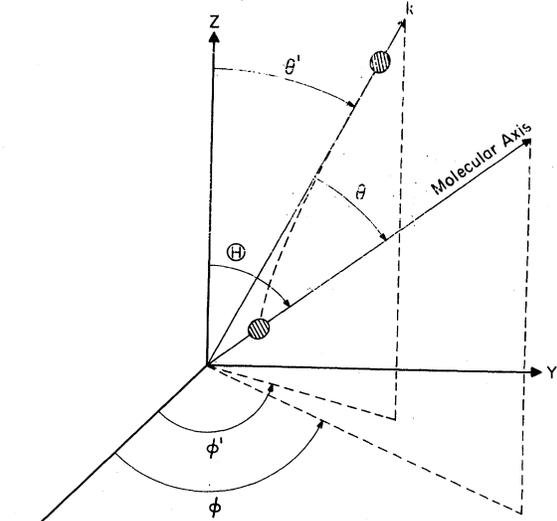


FIG. 2. Angular coordinates of initial molecular axis and wave vector \vec{k} of the dissociating particles relative to fixed axes.

Here k is the wave number of separating particles, $V_1(r)$ the internuclear potential of the $2p\sigma_u$ state, $\delta_{K'}$ the phase shift, and $P_{K'}(\cos \theta)$ are ordinary Legendre polynomials.

Though the phase shifts $\delta_{K'}$ could be solved for explicitly, this is unnecessary, since to terms of order $[(K'+\frac{1}{2})/kr]^2$ the factors $(-i)^{K'} \exp(i\delta_{K'})$ are independent²⁴ of K' , and the product may simply be expressed as a constant phase factor e^{iC} which drops out of the problem.

Use of the addition theorem²⁵ for spherical harmonics gives us

$$P_{K'}(\cos \theta) = \frac{4\pi}{2K'+1} \sum_{M'=-K'}^{K'} Y_{K'M'}^*(\theta', \phi') Y_{K'M'}(\Theta, \Phi), \quad (11)$$

so that

$$\xi_F = 4\pi \sum_{K'} \sum_{M'=-K'}^{K'} (-i)^{K'} e^{i\delta_{K'}} Y_{K'M'}^*(\Theta, \Phi) Y_{K'M'}(\theta', \phi') R_{kK'}(r). \quad (12)$$

Substituting Eqs. (4), (5), and (12) into Eq. (3) and summing over the initial M degeneracy, we get

$$d\sigma = [(4\pi)^2 \mu^2 v v / \hbar^3 c (2K+1)] \sum_{M, M', K'} \{ | \int \int Y_{KM}(\Theta, \Phi) Y_{K'M'}(\Theta, \Phi) \sin \Theta d\Theta d\Phi |^2 \\ \times [R_{nK}(r) R_{kK'}(r) Q_e'(r)] r^2 dr |^2 | Y_{K'M'}(\theta', \phi') |^2 \} d\Omega, \quad (13)$$

where $Q_e'(r) = e \int \psi_f^* \vec{n} \cdot \vec{z} \psi_i d\tau_e$. Integrating over solid angle to get σ , using the Hönl-London formulas²⁶ to perform the summations, and averaging over the angle between polarization and molecular axis, we get

$$\sigma_{nK} = [(4\pi)^2 \mu^2 \nu \nu / 3 \hbar^3 c] (1/2K + 1) [K |Q_{nK}^-|^2 + (K + 1) |Q_{nK}^+|^2], \quad (14)$$

where

$$Q_{nK}^\pm = \int_0^\infty R_{nK}(r) R_{k, K \pm 1}(r) Q_e(r) r^2 dr = \int_0^\infty \chi_{nK}(r) \chi_{k, K \pm 1}(r) Q_e(r) dr, \quad (15)$$

and

$$Q_e(r) = e \int \psi_f^* z \psi_i d\tau_e. \quad (16)$$

The radial functions $R_{k, K}(r)$ vary very slowly with K , and it is a good approximation to equate Q_{nK}^+ and Q_{nK}^- . We then have

$$\sigma_{nK} = [(4\pi)^2 \mu^2 \nu \nu / 3 \hbar^3 c] |Q_{nK}^0|^2, \quad (17)$$

where

$$Q_{nK}^0 = \int_0^\infty \chi_{nK}(r) \chi_{kK}(r) Q_e(r) dr. \quad (18)$$

Evaluating constants, and rewriting the expression in terms of the continuum energy ϵ and eigenenergy E_{nK} , we have

$$\sigma_{nK} = (\mu / \mu_{H_2^+})^{1/2} 2.60 \times 10^{-17} [(\epsilon + |E_{nK}|) / \epsilon^{1/2}] |Q_{nK}^0|^2. \quad (19)$$

Here σ_{nK} is in cm^2 , ϵ and E_{nK} in rydbergs, and all other terms are in atomic units. A factor $(1/k)^2$ from the coefficient of $\chi_{kK}(r)$ has been pulled outside the integral; and now normalization of $\chi_{kK}(r)$ is such that

$$\chi_{kK}(r) \rightarrow \sin(kr - \frac{1}{2}K\pi + \delta_K). \quad (20)$$

Bates¹⁶ has evaluated $Q_e(r)$ using "exact" electronic wave functions, and these values have been used in evaluating Q_{nK}^0 . The wave functions $\chi_{nK}(r)$ were calculated using a routine developed by Cooley²⁷ and modified by Zare and Cashion.²⁸ Equation (9) was solved for $\chi_{kK}(r)$ by outward integration, and normalization was performed by fitting Eq. (20) at large distances. The potential functions of Bates¹⁵ were used for $V_0(r)$ and $V_1(r)$.

Computations were first made by choosing values of ϵ (and thus k and λ) which occur at equally spaced values of the classical turning point along $V_1(r)$. Thus, values of ϵ and k were chosen which result from taking $0.05a_0$ intervals of r between $0.75a_0$ and $7a_0$. Cross sections were computed at each point for each of the 19 vibrational levels of H_2^+ and 27 levels of D_2^+ . The rotational quantum number K was taken to be $K = 1$ for H_2^+ and $K = 2$ for D_2^+ , since these are the dominant values for room-temperature samples of the respective species. One would not expect² the cross section to vary rapidly with K , since the first-order effect of changing K is to change $V_0(r)$ and $V_1(r)$ by approximately equal amounts.

Values of σ_{nK} at equal wavelength intervals were computed by a least-squares quadratic fit to the three nearest-neighbor points computed at equal r intervals. This was done for all vibrational levels at 25 Å intervals between 500 and 15 000 Å. The wavelength range extended as far as 300 to 10⁵ Å with the equal r interval data.

C. δ -Function Approximation to $\chi_{kK}(r)$

It is common practice¹⁸ to substitute a δ function at the classical turning point for $\chi_{kK}(r)$ in calculations involving dissociative states of molecules. It is instructive to perform the present calculation with this approximation in order to compare results with the "exact" calculation above.

For normalization⁵ of the δ functions we make use of the vibration sum rule applied to continuum states:

$$\int | \int \chi_{nK}(r) \chi_{kK}(r) dr |^2 \rho(\epsilon) d\epsilon = 1. \quad (21)$$

Setting $\chi_{kK}(r) = N\delta(r - r_c)$, we have

$$\int N^2 | \chi_{nK}(r_c) |^2 \rho(\epsilon) d\epsilon = 1.$$

If we now make use of the relationship between ϵ and r_c , setting $d\epsilon = [dV_1(r)/dr] dr = V_1'(r) dr$, and

make use of the fact that $\chi_{nK}(r)$ is normalized, we get

$$N^2 = 1/\rho(\epsilon) V_1'(r). \quad (22)$$

The expression for the cross section becomes, in this case,

$$\begin{aligned} \sigma_{nK} &= \frac{4\pi^2 (\epsilon + |E_{nK}|)}{3} \frac{1}{\hbar c} \frac{1}{V_1'(r_c)} |Q_e(r_c)|^2 |\chi_{nK}(r_c)|^2 \\ &= 2.69 \times 10^{-18} \frac{(\epsilon + |E_{nK}|)}{V_1'(r_c)} \\ &\quad \times |Q_e(r_c)|^2 |\chi_{nK}(r_c)|^2. \end{aligned} \quad (23)$$

Here ϵ and E_{nK} are in rydbergs, $V_1'(r_c)$ in Ry/a_0 , Q_e in units of ea_0 , $|\chi_{nK}(r_c)|^2$ in units of $1/a_0$, and σ_{nK} in cm^2 .

Evaluation of Eq. (23) for H_2^+ is readily performed by referring to Bates for¹⁵ $V_1(r)$ and for¹⁶ $Q_e(r)$, and to Cohen *et al.*²⁹ for $\chi_{nK}(r)$.

III. RESULTS AND DISCUSSION

The solid curves in Figs. 3 and 4 show the cross section as a function of wavelength for $n=0$ and $n=9$, respectively, as calculated using Eq. (19) for H_2^+ . The dashed curves show the results using the δ -function approximation; these cross sections are calculated using Eq. (23). Figures 5 and 6 show the corresponding results for D_2^+ , though no evaluation of Eq. (23) for $n=9$ was made for D_2^+ . As noted earlier, detailed results of all 46 cross sections are available elsewhere.¹⁹

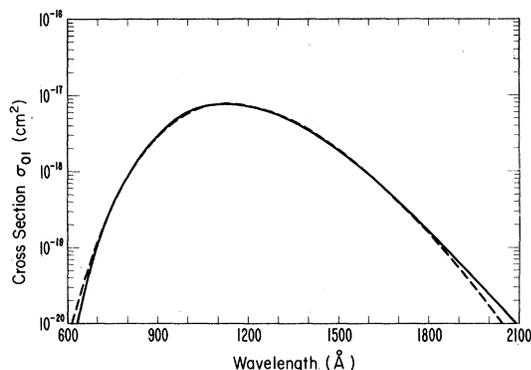


FIG. 3. The cross section as a function of wavelength for photodissociation of H_2^+ from the $n=0$ vibrational level. The solid curve shows the cross section calculated from Eq. 19 using accurate wave functions. The dashed curve is calculated from Eq. 23, where δ functions are used for the continuum radial wave functions.

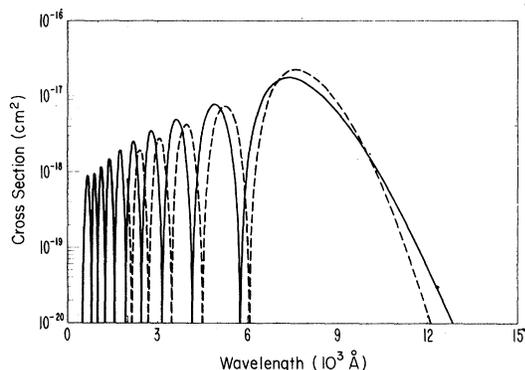


FIG. 4. The cross section as a function of wavelength for photodissociation of H_2^+ from the $n=9$ vibrational level. The solid curve shows the cross section calculated from Eq. (19) using accurate wave functions. The dashed curve is calculated from Eq. (23), where δ functions are used for the continuum radial wavefunctions.

The curves distinctively show how nodes and antinodes in the vibrational wave functions cause corresponding nodes and antinodes in the cross sections. The increase of successive maxima with increasing wavelength shows both the effect of the increase of $Q_e(r)$ with r and the increase of successive maxima of $\chi_{nK}(r)$. Increasing size of the $\chi_{nK}(r)$ functions as ϵ is decreased (λ increased) also contributes to this effect.

It is evident from Figs. 3 and 5 that the δ -function approximation gives results very close to the true values for the zeroth vibrational levels. Figure 4 shows, however, that when high vibrational quantum numbers are involved, one cannot rely on this approximation. Thus, though we see that the qualitative aspects are much the same and the general magnitude is much the same, the nodes and antinodes are actually out of phase with one another over some wavelength ranges. At some specific wavelengths the error can be orders of magnitude. This conclusion has been pointed out before.¹⁸

The isotope effect for a given vibrational level is clearly seen by comparing Figs. 3 and 5 with Figs. 4 and 6, respectively.

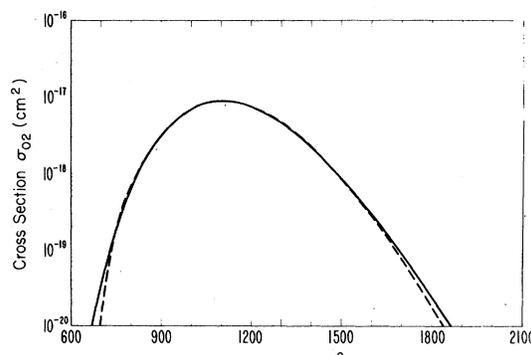


FIG. 5. The cross section as a function of wavelength for photodissociation of D_2^+ from the $n=0$ vibration level. The solid curve shows the cross section calculated from Eq. (19) using accurate wave functions. The dashed curve is calculated from Eq. (23), where δ functions are used for the continuum radial wavefunctions.

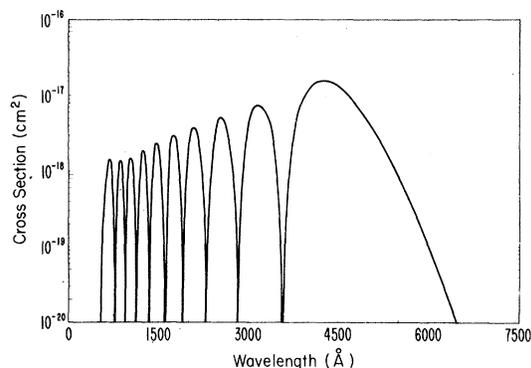


FIG. 6. The cross section as a function of wavelength for photodissociation of D_2 from the $n=9$ vibration level. The cross section is calculated from Eq. (19) using accurate wave functions.

In arriving at Eq. (13), we have summed over initial M states. In practice, of course, there may be a distribution of n and K states as well, in which case we have

$$\sigma = \sum_{n,K} p_{nK} \sigma_{nK}, \quad (24)$$

where the p_{nK} 's are population factors for the different levels.

In the experiment to be described in a later publication,¹³ H_2^+ ions are formed by electron bombardment of H_2 , and it is reasonable to assume a first approximation for the p_{nK} 's to be normalized Franck-Condon factors³⁰ between H_2 and H_2^+ . If we make this assumption and the assumption that only dominant K values contribute as discussed above, we get the predicted cross sections shown in Fig. 7 for H_2^+ and D_2^+ . The predicted curve of Oksjuk¹⁴ for H_2^+ is also shown for comparison.

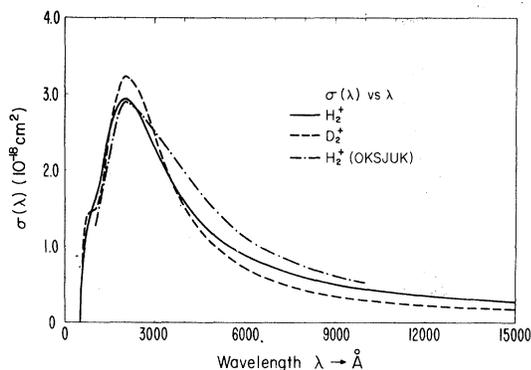


FIG. 7. The cross section as a function of wavelength for photodissociation of H_2^+ (solid curve) and D_2^+ (dashed curve) when the populations of vibrational levels of the molecular ion are given by the normalized Franck-Condon factors between H_2 (D_2) and H_2^+ (D_2^+). A calculation due to Oksjuk¹⁴ for H_2^+ is shown by the dot-dashed curve.

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† Of the National Bureau of Standards and the University of Colorado, Boulder, Colo.

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The latter has used Morse curves for $V_0(r)$ and $V_1(r)$ and Franck-Condon factors calculated by Hiskes.³¹ It is difficult to assess the relative contributions of these differences to the disagreement between curves; but Hiskes' Franck-Condon factors are quite different from others,³⁰ and Morse curves are notably poor^{30, 32, 33} for getting accurate vibrational overlaps between states.

The σ_{nK} values from these computations along with experimentally measured σ 's will form systems of equations such as Eq. (24), which one should be able to solve for the p_{nK} 's. This may be a useful diagnostic tool when one is interested in vibrational relaxation of H_2^+ in collisions or when one is interested in internal energy states when H_2^+ is formed from various parent molecules.

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Concerning the Stability of the Negative Ions H^- and Li^- *

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The unrestricted Hartree-Fock (UHF) wave functions for H^- and for Li^- have the $Z+1$ th electron at infinity, and thus have the same energy as the neutral atoms. That is, the stability of these negative ions is not accounted for by Slater determinant wave functions, not even if the orbitals are allowed to split. We show that the difficulty here is that the UHF wave functions do not have the proper spin symmetry. If the Slater determinant is spin-projected and the orbitals optimized after projection (to obtain what is called the GF wave function), these negative ions are predicted correctly to be stable. Since the GF wave function leads to an independent particle interpretation, we see that instantaneous polarization of the neutral-atom orbitals by the $Z+1$ th electron is *not* crucial to the stability of these negative ions. From an analysis of the differences between the UHF and GF wave functions, we find that the key term leading to stability of the negative ions is an exchange term (particularly the nuclear attraction part of this term), just like the exchange term important in the valence-bond wave function of H_2 .

INTRODUCTION

A number of negative ions (e. g., H^- , Li^- , C^- , O^- , and F^-) are known to be stable.¹ However, because of the greater importance of electron-electron repulsion for these systems, simple wave functions may not always account for the stability of these ions. For example, for H^- , Li^- , and O^- , the Hartree-Fock wave function leads to a higher energy for the ion than for the neutral atom.² In this case it becomes of interest to consider improved wave functions for two reasons. One, if we are to believe the properties predicted by a wave function for a system, we should like for the wave function to be good enough at least to correctly predict the stability of the system. And two, it is of theoretical interest to determine and understand physically why the Hartree-Fock and other methods cannot account for stability of negative ions.

This can be approached by examining better types of wave functions until we obtain a type which can correctly predict stability.

The negative ion has more electrons than protons; thus we expect one electron to be very loosely bound and to be in a rather diffuse state. Hence it is possible that the *average* potential due to the other Z electrons and the nucleus of charge Z might not be strong enough to bind the $Z+1$ th electron.³ In this case it would be the instantaneous polarization of the other electrons which is primarily responsible for allowing a deep enough potential to bind the $Z+1$ th electron.³ We will denote this possibility as explanation I. In the HF method each orbital is adjusted only for the *average* potential due to the other electrons. Thus explanation I could account for the incorrect description by the HF method of such ions as H^- , Li^- , and O^- .

However, the HF method has an additional