PHYSICAL REVIEW B VOLUME 19, NUMBER 4 15 FEBRUARY 1979

Scattering of molecular and atomic hydrogen ions from single-crystal surfaces

W. Heiland, U. Beitat, and E. Taglauer
EURATOM-Association-Max-Planck-Institut für Plasmaphysik, D-8046 Garching, Federal Republic of Germany

(Received 4 August 1978)

Energy spectra of $H_2{}^+$ molecules and of the resulting H^+ ions backscattered from Ni(111) and W(100) surfaces are measured for incident $H_2{}^+$ molecules in the energy range from 200 eV to 2 keV. Comparison is made to spectra obtained from incident H^+. It is shown that the dissociation of the impinging molecular ions is not caused by an electron-loss process, but proceeds via excited molecular states. The dissociation probability may depend on the surface structure, which is concluded from pronounced changes of the ion yields with the orientation of plane of scattering relative to the crystal surface.

In many ion-bombardment experiments with hydrogen as projectile molecular ions are used to achieve higher current densities at lower incident energies per proton. The experimental evidence in sputtering,[1] charge-state fraction,[2] or proton emission[3] is that, in general, an H_2^+ ion behaves like two independent protons at half the accelerating voltage. These observations are made above a few kilo-electron-volts. It has been shown that at energies below a few kilo-electron-volts the survival of molecular ions may not be negligible.[4] Since we are involved in experiments on desorption by ion impact[5] in the energy range from 100 eV to 2 keV, this question is of experimental interest. On the other hand, no experiments (besides the one mentioned[4] at 5 keV) have been reported in the energy range down to 100 eV. We conducted experiments using H_2^+ as molecular projectile impinging on Ni(111) and W(100) surfaces.

I. EXPERIMENT

The experimental setup has already been described.[6] It is a UHV system equipped with a four-grid low-energy electron diffraction Auger system and an ion scattering facility. It consists of an electron impact ion source followed by a mass separator. The energy distribution of the scattered ions is measured at variable scattering angles by means of an electrostatic analyzer which can rotate around the target axis. With hydrogen as projectile target current densities of 10^{-7} A/cm^2 H_2^+ and 10^{-6} A/cm^2 H^+ can be produced, keeping the pressure in the target chamber in 10^{-10}-Torr range. Primary beam measurements (Fig. 1) are taken with reduced current. Sorption of H on the targets during the measurements cannot be excluded and there is no direct way to measure this possible contamination. Other contaminants are measured to be lower than a few hundredths of a monolayer.

II. RESULTS

Figures 1 and 2 show energy spectra obtained for the bombardment of Ni(111) and W(100) with H_2^+ and H^+ at an accelerating voltage of 600 eV. Also shown are the H^+ parts of the spectra when the incident H_2^+ ions are accelerated by 1200 eV. The main results from this type of measurements are: (i) The yield (peak area) of H_2^+ ions is of the order of a few percent compared with the yield of H^+ ions which result from dissociation of the same H_2^+ beam, (ii) the full width at half-maximum (FWHM) of the H_2^+ peak is smaller compared with the FWHM of the H^+ spectrum resulting from incident H^+ at the same accelerating voltage, (iii) the latter peak has again a smaller width compared with the H^+ peak resulting from H_2^+ bombardment at twice the accelerating voltage, (iv) the H_2^+ peak is shifted to lower energies compared with the H^+ peak at the same accelerating voltage, and (v) the H^+ peak from H_2^+ at twice the accelerating voltage is shifted towards higher energies. These shifts of the peak positions at FWHM are below 2 eV. These observations are based on measurements from 100 eV to 2 keV and for scattering angles from 5° to 90°. Figures 1 and 2 serve as examples.

Measurements at different energies and laboratory scattering angles are summarized in Fig. 3 with respect to the H_2^+ survival. For different ratios of the molecular-ion yield to total-ion yield it is possible to define "molecular survival" and "dissociation" regions. As expected, the chances of surviving increase with decreasing energy or decreasing scattering angle.

Understanding of the observed data is complicated not only by the neutralization usually encountered in this energy range,[7] but also owing to the low energies and small impact angles by plural scattering or surface channeling. Figure 4 shows the ion yield from W(100) as a function of the angle of the orientation of the plane of scattering

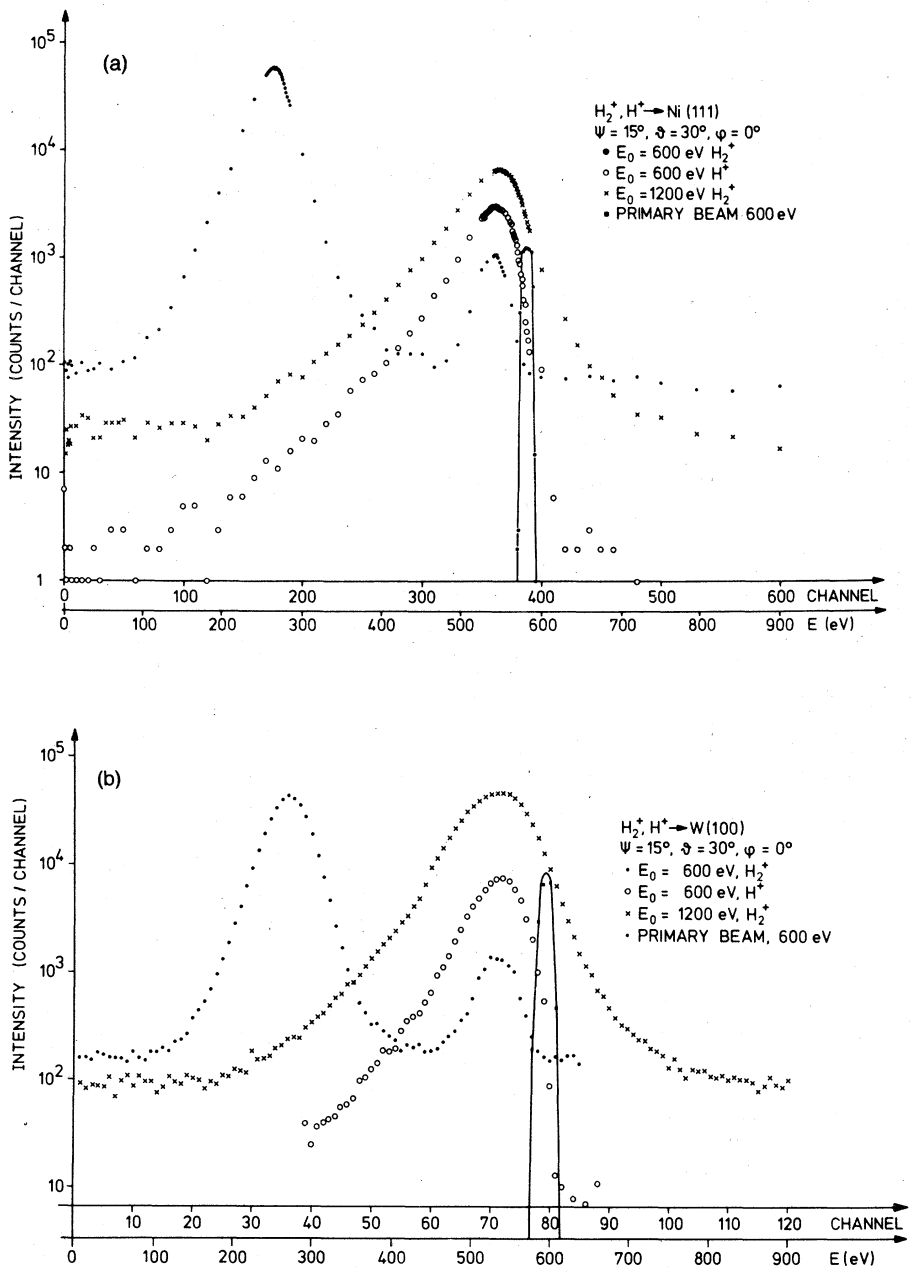

FIG. 1. Energy spectra of H^+ and H_2^+ scattered from Ni(111) (a) and W(100) (b), when bombarded with H^+ (open circles) or H_2^+ (dots and crosses). Also shown is the energy distribution of the primary beam. (The increased background for the spectra obtained from H_2^+ bombardment is due to an increased sampling time in order to achieve sufficient counts in the H_2^+ peak). ψ is the angle of incidence towards the surface, ϑ is the laboratory scattering angle. Scattered species are H^+ and H_2^+, incident energies are 600 eV (H^+ and H_2^+), 1200 eV (H_2^+ only). For H_2^+ bombardment two peaks are observed, one near the primary energy is surviving H_2^+, the second at about half the energy is H^+.

relative to the crystal orientation. There is pronounced "focusing" in the [100] and [110] surface directions. The H^+ result is probably not due to a change in ion survival probability since it can be simulated by MARLOWE[8] without taking neutralization into account. As expected, the effect is less pronounced for the relatively smooth Ni(111) surface.

III. DISCUSSION

The main experimental information which we have for understanding the survival or dissociation of the H_2^+ are the energy spectra. The energy of a proton or hydrogen atom originating from a dissociation process is given (in the laboratory system) by

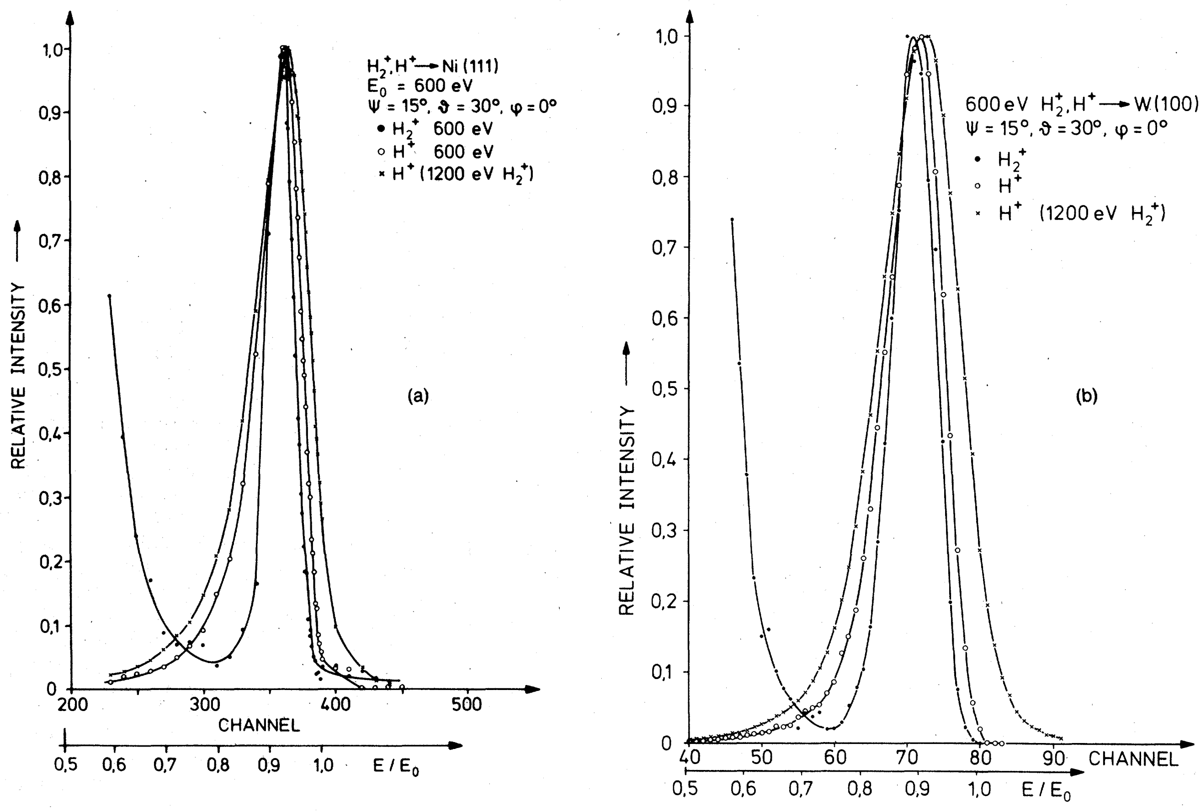

FIG. 2. Part of the energy spectra of Fig. 1 in linear scale after background subtraction and normalizing the peak height.

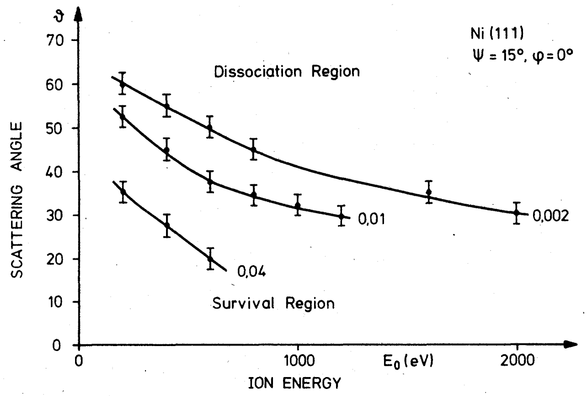

FIG. 3. Curves of constant ratio of backscattered ion yield, H_2^+ to $H^+ + H_2^+$, as function of laboratory scattering angle and primary energy of the incident H_2^+ ion. Lines are drawn to guide the eye.

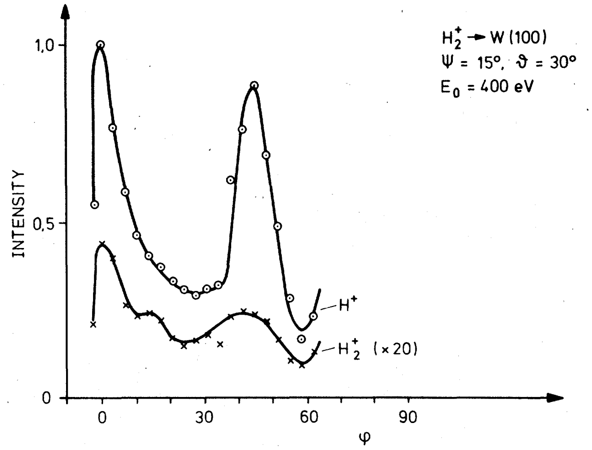

FIG. 4. Ion yield of H^+ and H_2^+ from a W(100) surface bombarded with H_2^+ at primary energy of 400 eV as a function of the azimuthal angle φ. Angle of incidence towards the surface $\psi = 15°$, laboratory scattering angle $\vartheta = 30°$. At $\varphi = 0°$ the plane of scattering is parallel to a [100] surface direction, at $\varphi = 45°$ parallel to [110].

$$E_{\text{lab}} = \tfrac{1}{2}E_{\text{beam}} + \tfrac{1}{2}E_{\text{rep}} \pm (E_{\text{beam}}E_{\text{rep}})^{1/2}\cos\theta\ , \qquad (1)$$

where θ is the angle between the beam direction and the molecular axis, and E_{rep} is the repulsive energy acting between the particles resulting when dissociation occurs. For two protons at the distance they have in an H_2^+ molecule, i.e., 1.06 Å, one has $E_{\text{rep}} = 13.6$ eV. In our experiment we face the problem that the particles undergo several collisions, such that dissociation may occur at any point of the trajectory across the surface. After dissociation further collisions of the product particles can be expected. Finally, we measure only the positive ions which survive, the flux of neutral H and that of possibly existing H^- and H_2 being unknown. Extrapolations from experiments at higher energies give estimates for the charge-state fraction (H^+ to $H^0 + H^+ + H^-$) in the 10^{-3} range; for H^- the value may be of the same order of magnitude.[2,9] However, at low energies and grazing angles the energy spectra are not necessarily influenced by neutralization[10] (see also Fig. 5 below). By varying the crystal thickness in the computer experiment it becomes evident that only the top two layers contribute significantly to backscattering, e.g., in the open channel directions [100], whereas in "random" directions essentially all reflected particles have not penetrated beyond the top layer.

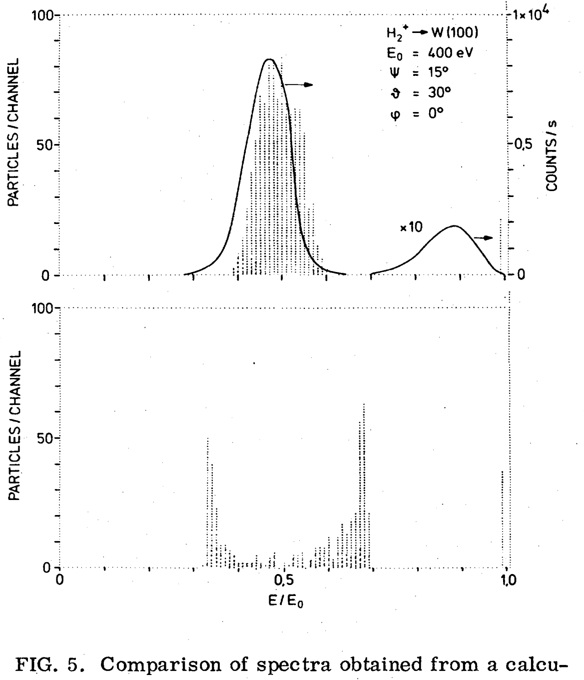

FIG. 5. Comparison of spectra obtained from a calculation using the program MARLOWE (Ref. 8) (histograms) with an experimental spectrum [line, 5(a)]. For the upper histogram [5(a)] an energy distribution is used for the repulsion energy E_{rep} of the dissociating molecule (Fig. 6), for the lower part [5(b)] a constant energy $E_{\text{rep}} = 13.0$ eV.

These observations allow the construction of a program within the MARLOWE system to simulate the effects of dissociation. This is achieved by introducing mainly two new parameters, i.e., the repulsive energy E_{rep} and a disintegration distance D. The incoming particle has mass 2 and atomic number 2. It scatters along the surface until it crosses the plane located at the distance D above the ion cores of the top layer. It then disintegrates at the next collision. From there on the particle will be a $m = 1$, $Z = 1$ particle. It initially has the direction of the previous $m = 2$, $Z = 2$ particle, but its energy and direction will be changed according to formula (1), where θ is selected at random. It turns out that by varying the distance D the survival rate of the $m = 2$, $Z = 2$ particle can be adjusted, without great changes in the energy spectra. By varying E_{rep} the shape of the energy spectra of the dissociated particles can be formed.

The physical model justifying this approach starts from the experimental observation that the energy spectra obviously do not reflect a repulsive energy of 13.6 eV [formula (1)], as is the case at high energies,[11,12] where dissociation is caused by Coulomb repulsion after the electron from H_2^+ is lost. Secondly, we know from experience that electron pickup is the most likely process in our energy range. So roughly at about 2–3 Å above the surface the incoming ion (H_2^+) will be neutralized either into the ground state (Auger neutralization) or into an excited state (resonance neutralization).[13] If the latter is antibonding, the molecule will fall apart independently of further scattering events; if not, subsequent collisions will provide the opportunity for electronic, vibrational and rotational excitation, which may lead to dissociation. All these effects are not included in our simulation which provides a sufficiently randomized source of protons along the trajectories of the incoming particle only.

As a result of the computer experiments Fig. 5 shows energy spectra in comparison with the experiment. The agreement between the experimental H^+ peak and the computed H peak is good, as far as peak width and peak form are concerned, for the case shown in Fig. 5(a). There the repulsive energy E_{rep} [Eq. (1)] is chosen at random from an energy distribution which starts at zero and falls off to higher energies according to a gaussian distribution with a width $\sigma = 2.0$ eV. θ is chosen at random and the split occurs after crossing the plane at $D = 1.20$ Å. This then results in a mean split distance of 1.04 Å, with a

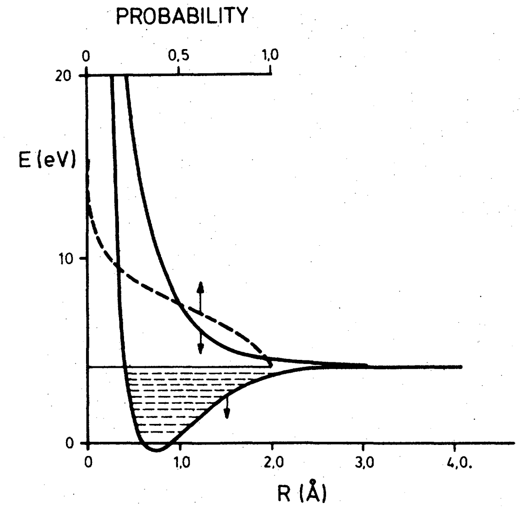

FIG. 6. Distribution of repulsion energies E_{rep} (dashed line) used in Fig. 5(a) compared with the potential energy of H_2 in the ground state and an excited state (thin dashed lines are vibrational levels).

rms deviation of 0.012 Å. For comparison Fig. 5(b) shows the energy spectrum obtained for a sharp energy $E_{\mathrm{rep}} = 13$ eV. The two-peak structure typical for a dissociation due to Coulomb explosion[11,12] prevails for all repulsion energies greater than 0.5 eV, even when we choose an energy distribution around E_{rep}. With 0.5–1.0 eV as repulsion energy we could match the total width of the experimental spectra. Figure 6 shows the energy distribution used for Fig. 5(a) which is a crude approximation of any possible population of the vibrational levels folded with an antibonding potential curve.[14] In the nomenclature of atomic physics the process is called "dissociative recombination."[15] There is a spectrum of possibilities to dissociate either H_2^+ or H_2. The situation is further complicated at the surface owing to the plural scattering and the possibility of deexcitation via resonance ionization.[13,16]

The discrepancy between the simulated spectrum and the experiment for the H_2^+ peak [Fig. 5(a)] is not surprising, since we actually made no attempt to describe the molecular ion properly. Nevertheless the experiment shows clearly that the H_2^+ molecule survives total energy losses (elastic plus inelastic) which are large compared with the dissociation energy [up to 100-eV energy loss versus 2.65-eV dissociation energy,[17] e.g., at 400 eV, Fig. 5(a)]. This observation has been discussed previously.[4] Within our model inelastic loss mechanisms are possible via excited states of the neutral molecule (excited states of the ion are essentially unstable[14,18].) By a resonance ionization process a transition from an excited neutral into the groundstate of the molecular ion may be possible.

The azimuthal dependence of the ion yields (Fig. 4) can partly be explained by the elastic scattering process. The surface structure of the W(100) causes "focusing" of the particles in the [100] ($\varphi = 0$) and [110] ($\varphi = 45°$) directions. This effect is less pronounced for the relatively large H_2^+ molecules. With MARLOWE we can reproduce the azimuthal H-intensity pattern in general agreement with the experiment. However, the maximum for $\varphi = 45°$ is about 0.15 of the maximum at $\varphi = 0°$ in contrast to the experiment, where these are about of equal height. This discrepancy suggests that there is also azimuthal variation of the inelastic process, which may enhance the H^+ yield in the [110] direction. This could reflect variations in the ion yield of the H^+, as observed at higher energies for Ar^+ scattered from Cu,[19] as well as a higher dissociation yield of the H_2^+ in the "bumpier" [110] surface rows (channels) in comparison with the [100] direction.

---

[1] R. Weissman and R. Behrisch, in *Ion Surface Interaction, Sputtering and Related Phenomena*, edited by R. Behrisch, W. Heiland, W. Poschenrieder, P. Staib, and H. Verbeek (Gordon and Breach, London, 1973), p. 55.

[2] W. Eckstein and F. E. P. Matschke, Phys. Rev. B 14, 3231 (1976).

[3] E. O. Rausch and E. W. Thomas, Phys. Rev. A 14, 1912 (1976).

[4] W. Eckstein, H. Verbeek, and S. Datz, Appl. Phys. Lett. 27, 527 (1975).

[5] E. Taglauer and W. Heiland (unpublished); see, e.g., W. Heiland and E. Taglauer, Inst. Phys. Conf. Ser. 38, 287 (1978).

[6] E. Taglauer, W. Melchior, F. Schuster, and W. Heiland, J. Phys. E 8, 768 (1975).

[7] W. Heiland and E. Taglauer, Nucl. Instrum. Meth. 132, 535 (1976).

[8] M. T. Robinson and I. M. Torrens, Phys. Rev. 93, 5008 (1974).

[9] H. Verbeek and W. Eckstein, *Proceedings of the Seventh International Vacuum Congress and Third International Conference on Solid Surfaces*, Vienna, 1977, edited and published by R. Dobrozemsky, L. F. Rüdenauer, F. P. Viehböck, and A. Breth (Vienna, 1977), p. 1309.

[10] W. Heiland, E. Taglauer, and M. T. Robinson, Nucl. Instrum. Meth. 132, 655 (1976).

[11] J. Golovchenko and E. Laegsgaard, Phys. Rev. A 9, 1215 (1974).

[12] J. W. Tape, W. M. Gibson, J. Remillieux, R. Laubert, and H. E. Wegner, Nucl. Instrum. Meth. 132, 75 (1976).

[13] H. D. Hagstrum, in *Inelastic Ion-Surface Collisions*, edited by N. H. Tolk, J. C. Tully, W. Heiland, and C. W. White (Academic, New York, 1977), p. 1.

[14] T. E. Sharp, At. Data 2, 119 (1972).

[15] See, e.g., D. Auerbach, R. Cacak, R. Candano, T. D. Gaily, C. J. Keyser, J. Wm. McGowan, J. B. A. Mitchell and S. F. J. Wilk, J. Phys. B 10, 3797 (1977);

M. Vogler and G. H. Dum, Phys. Rev. A 11, 1983 (1975); B. Peart and K. T. Dolder, J. Phys. B 7, 236 (1974).

[16] T. P. Grozdanov and R. K. Janev, Phys. Lett. A 65, 396 (1978).

[17] A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, London, 1968).

[18] E. Teller, Z. Phys. 61, 458 (1930).

[19] W. F. von der Weg and D. J. Bierman, Physica 44, 177 (1969).