Light-Ion Charge Exchange in Atmospheric Gases*

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Measurements of the total charge-exchange cross sections of H^+, H_2^+, and He^+ in N_2, O_2, CO_2, and H_2O have been made, using a collision chamber to collect the slow collision products. An energy range from 40–1500 eV was examined. Except for protons incident on N_2 and O_2, the processes examined have cross sections which continue to rise at energies below 200 eV; some collision products were found to have energies of several eV. Excited states must be invoked to explain the observed results in terms of the adiabatic criteria. Comparisons with earlier work are given.

INTRODUCTION

AS part of a program to study charge-exchange processes for light ions, measurements have been made of total charge-exchange cross sections for H^+, H_2^+, and He^+ incident on N_2, O_2, CO_2, and H_2O in the energy range 40–1500 eV. Such reactions are of interest in the upper atmosphere, in the atmospheres of planets where the absence of a magnetic field would allow direct bombardment by the solar wind, and in laboratory situations where these species may be present, perhaps as impurities. These investigations also serve to clarify the general applicability of the "adiabatic theory" for charge exchange,[1] which predicts cross-section maxima when the condition $v = a|\Delta E|/h$ is satisfied, where v is the incident ion velocity, a is a distance of about 7 Å, and $|\Delta E|$ represents the energy difference between the initial and final states. In a previous investigation[2] (paper I), an earlier version of the present apparatus was used to measure the charge-exchange cross sections of H^+, H_2^+, and He^+ incident on H_2, Ar, Kr, and Xe; that work confirmed that excited electronic states of monatomic ions had to be considered in applying the adiabatic theory to charge-exchange processes, as postulated by other investigators.[3] The present paper examines charge exchange by ions undergoing interactions with molecules, where dissociations, as well as the production of excited states, may occur. Although it is generally assumed that the adiabatic theory should apply to such processes, the complexity of molecular systems makes it difficult to predict the value of $|\Delta E|$ for this class of reactions.

Some of the collision cross sections reported in this paper have also been measured previously.[4–10] As dis-

cussed below, the earlier work contains some discrepancies; some earlier measurements also depend on a transfer of an absolute value to a set of relative measurements. It is hoped that the results reported here resolve some of the previous uncertainties and may serve as a guide to theoretical treatments of ion-molecule collision phenomena.

APPARATUS

The apparatus used in the present investigation is a modification of the experimental equipment described in I. As shown in Fig. 1, ions were produced in a rf discharge and then extracted, accelerated, and focused into a 127° electrostatic energy analyzer followed by a cross-field velocity filter. For the present work, the internal elements of the source and analysis systems were shielded from the external grounded vacuum chamber walls; the shields, the magnetic yoke in the velocity selector, one side of the ion source power supply, and the midline reference potentials of the analyzer, deflection, and focusing electrodes were all connected together and to an adjustable bias potential which could be made positive or negative with respect to ground. Relative to this adjustable potential, the ion beam traversed the analyzers with an energy of about 500 eV. As the adjustable bias potential was varied, the beam gained or lost energy in passing from the velocity selector to the collision chamber, which was at ground potential. The energy transition was governed by a lens system similar to that used by Lindholm.[11] It was found that the energy of the beam entering the collision chamber could be varied from less than 40 eV to above 1500 eV with less than one order of magnitude of difference between the currents at the highest and lowest energies. Furthermore, this range of energies could be obtained with only minor readjustments of the analyzing and focusing voltages. This behavior was in favorable contrast to that obtained with the apparatus

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[11] Diagram may be found in J. B. Hasted, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 705.
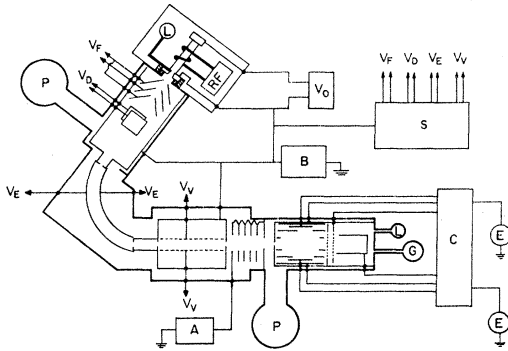
FIG. 1. Diagram of apparatus. RF, radio-frequency oscillator; V_0, acceleration voltage; B, bias for varying beam energy; S, supply for deflection, focusing, and analyzing voltages; V_D, deflection voltages; V_F, focusing voltages; V_E, energy analyzer voltages; V_V, velocity selector voltages; A, voltage supply to acceleration-deceleration lens assembly; C, collision chamber control unit; E, electrometers; L, gas inlets; G, pressure gauges; P, diffusion pumps. The heavy dots represent insulating feed-throughs.

FIG. 3. Plot of incident beam current as a function of retarding potential. The increase between 0 and 80 V is caused by secondary electrons; the dashed curve gives the beam energy distribution.

used in I, where the beam varied by three orders of magnitude over a smaller energy range and a more complex array of controls was required for beam alignment.

The collision chamber used in the present investigation employed weak transverse electric fields to collect low-energy charged collision products, similarly to that used in I, but was designed to give a longer collection length, more uniform collection fields, and a greater flexibility in obtaining information on the collected current as a function of field strength. Details of the collision chamber and the associated circuitry are shown in Fig. 2. An array of 10 parallel plates, 0.25 mm thick and separated by 3.6 mm, were mounted on insulators. The centers of plates 3–8 were cut away to form the body of the collision region. All but plates 2 and 9 were connected across a dropping resistor chain
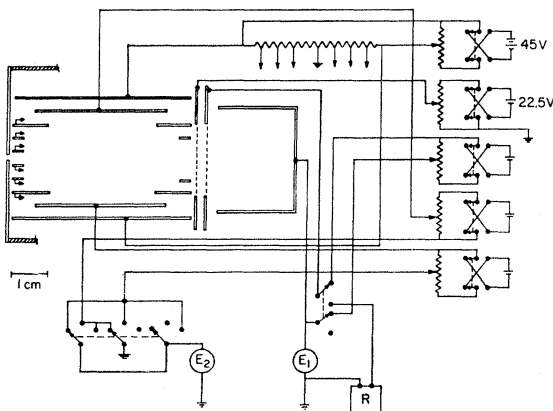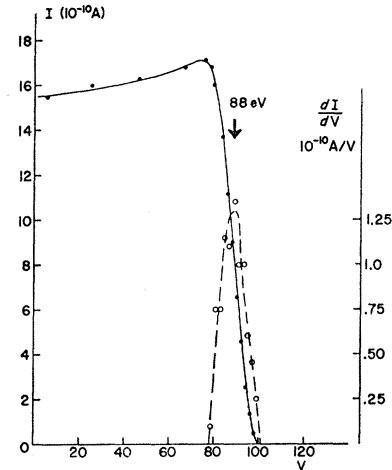

FIG. 2. Details of collision chamber and circuits for applying collection fields and retarding voltages. Electrometer E_1 measures the incident beam current; E_2 measures the current collected by the top, bottom, or both collection plates; R is the retarding voltage supply for measuring the beam energy.

which was grounded in the center and chosen so that a reversible uniform electric field variable from 0 to 18 V/cm could be applied. Separate circuits supplied the voltage applied to plates 2 and 9, which collected the currents representing the charged collision products originating along a 3-cm path length in the collision chamber. A 3-deck switching array made it possible to observe the current collected by each plate separately or the net collected current to both plates; the latter arrangement yielded automatic compensation for ionization or secondary electron production which might otherwise affect the charge-exchange measurements.

The primary ion beam, after entering the collision chamber through a 3-mm-diam opening at the front and traveling through the 3-cm-long region between the collection plates, passed through a 95% transparency tungsten mesh, usually maintained at ground potential. This first grid separated the transverse collection fields from the field produced by the negative secondary electron suppression potential applied to the second mesh grid that was located in front of the Faraday cup which collected the primary beam. The second grid could be alternatively connected to an external potential which could be varied to block the primary beam and therefore to determine its energy. Figure 3 presents a typical result of a beam-energy measurement. It should be noted that the limitation on the lowest beam energy examined was set not by the ion source and analysis system but rather by the collision chamber collection field. At the lowest energies attainable, the transverse collection field required to sweep up the collision products would also deflect the primary beam, so that it would not enter the Faraday cup.

Gases were admitted to the collision chamber through a leak valve and escaped only through the aperture through which the beam entered. Pressures were

measured with a Varian milliTorr gauge which was calibrated against an MKS Instruments capacitance manometer.

EXPERIMENTAL PROCEDURE

The procedure used to obtain and analyze the data has been explained in I; in brief, the primary current I_0 and the net collected current I_c were recorded as functions of collision-chamber pressure; a computer routine calculated the cross section σ from a least-squares fit based on the relation $I_c/I_0 = Nl\sigma$, where N is the gas number density and l is the collection length. Measurements were made over the attainable energy range on two separate days; the two sets of results were averaged to obtain the values presented in this paper.

The results are believed to be accurate to $\pm 15\%$, with the exception of the low-energy cross sections for processes yielding energetic products, particularly for the process $He^+ + O_2$. It is not certain if all the collision products for this process were collected. This difficulty became apparent when measurements were made of the currents to the two collection plates, separately and together, as a function of collection field and gas pressure, for a few selected reactions and beam energies. The results of two such studies are shown in Figs. 4 and 5. The symmetry of collection as the direction of the field is reversed is evident. As expected, the net current collected by both plates simultaneously is the algebraic sum of the currents measured for each of the plates separately. The negative current observed to the electron collecting plate is mainly due to secondary elec-
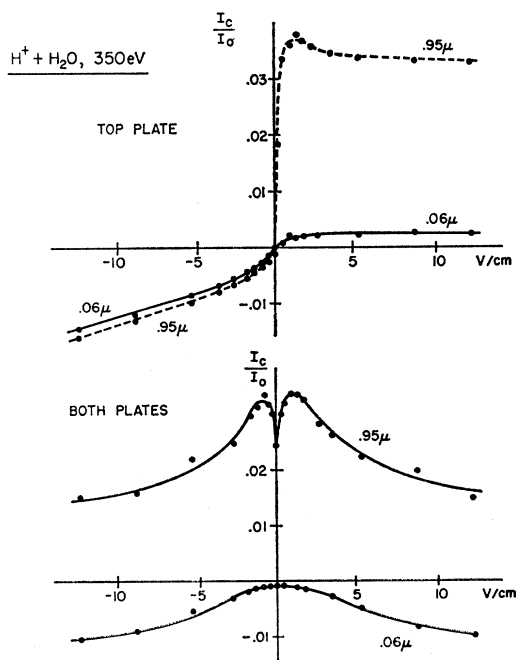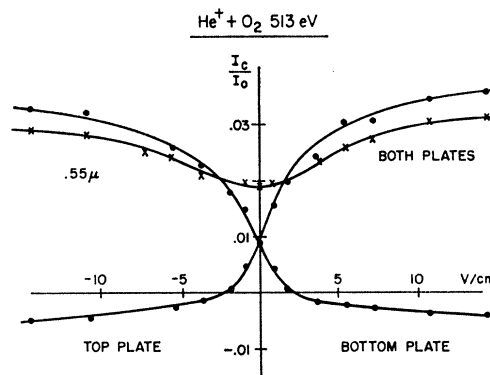
FIG. 5. Study of the collected current as a function of collected field for the $He^+ + O_2$ reaction at 0.55×10^{-3} Torr. Curves obtained at 0.05×10^{-3} Torr were about two orders of magnitude smaller and are not shown.

trons from the primary beam; it is nearly pressure-independent and does not affect the analysis of the data. In Fig. 4, it can be seen that a field of about 4 V/cm is adequate to insure saturated collection of the collision products. In Fig. 5, however, complete collection saturation does not occur. Further discussion of this effect is given later.

RESULTS AND DISCUSSION

Figures 6–10 display the results obtained in this investigation; comparisons to previous work are also shown.

Oxygen

Total charge-exchange cross sections for protons on oxygen molecules have been previously been measured in a crossed-beam experiment, yielding relative values over an energy range 40–10 keV; normalization was made using absolute values measured at a few higher energies.[12] It can be seen that the agreement between the present measurements and the earlier published
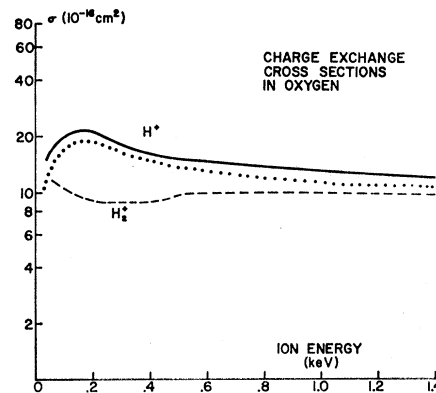
FIG. 4. Study of the collected current as a function of collection field for the $H^+ + H_2O$ reaction.

FIG. 6. Charge-exchange cross sections for H^+ and H_2^+ in oxygen gas. Solid curve, present results for H^+; dotted curves, Stebbings et al. (Ref. 9); dashed curve, present results for H_2^+.

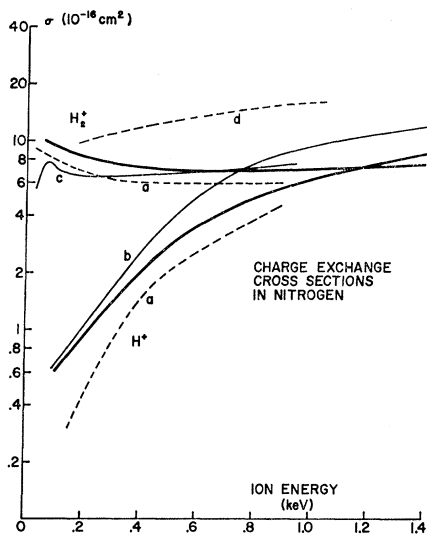[12] P. M. Stier and C. F. Barnett, Phys. Rev. **103**, 896 (1956).

FIG. 7. Charge-exchange cross sections for H^+ and H_2^+ in nitrogen gas. Heavy curves, present work; a, Gustaffson and Lindholm (Ref. 6); b, Gilbody and Hasted (Ref. 5); c, Wolf (Ref. 4); d, Ghosh and Sheridan (Ref. 7).

results is good, easily within the expected experimental limits of accuracy. The 12.2-eV ionization potential of O_2 and the resulting $|\Delta E| \simeq 1.36$ eV would suggest a cross-section maximum at about 200 eV. The actual maximum is only slightly lower; the decrease observed at energies below 150 eV indicates that the predominant process observed is probably $H^+ + O_2 \rightarrow H + O_2^+$, with the O_2^+ being formed in the ground state. The differential charge-exchange cross section for this process has also been studied[13]; it has been found that at most a small part of the energy defect is transferred to the proton transverse to its motion. An excitation of O_2^+ vibrational states has been suggested as a sink for the energy difference between the initial and final states.

The cross section for $H_2^+ + O_2$ is found to rise at decreasing energies; the data also suggest that a second maximum may exist at a few keV. The second maximum could be associated with the production of ground state O_2^+, with $|\Delta E| \approx 3.5$ eV, but the increase of cross section for energies below 200 eV suggests reactions involving excited molecular levels must be occurring.

The cross section for He^+ on O_2 is found to be similar in form to that reported in Ref. 10, but about 20% smaller. Examination of Fig. 5 indicates that the ions were produced with energies in the range 10–20 eV; even the maximum collection field (18 V/cm) was not adequate to insure that $\sim$100% collection efficiency was attained. Particularly at the lowest energies, an upward adjustment of the results by perhaps 30–50% would be appropriate. The reader is referred to Ref. 10 for evidence that the predominant reaction occurring is $He^+(^2S) + O_2(X^3\Sigma) \rightarrow He(^1S) + O_2^+(c^4\Sigma_u)$, followed by dissociation to produce $He + O + O^+$.

[13] H. H. Fleischmann, R. A. Young, and J. W. McGowan, Phys. Rev. **153**, 19 (1967).

Nitrogen

The cross section for the process $H^+ + N_2$ obtained in the present investigation is in good agreement with the results published by Gilbody and Hasted and by Gustaffson and Lindholm. The latter investigators made a mass analysis of the collision products which indicated that $H^+ + N_2 \rightarrow H + N_2^+$ is the predominant reaction. It is probable that N_2^+ in the $X^2\Sigma_g^+$ ground state (15.58 eV) is formed, resulting in $|\Delta E| = 2.02$ eV. Such
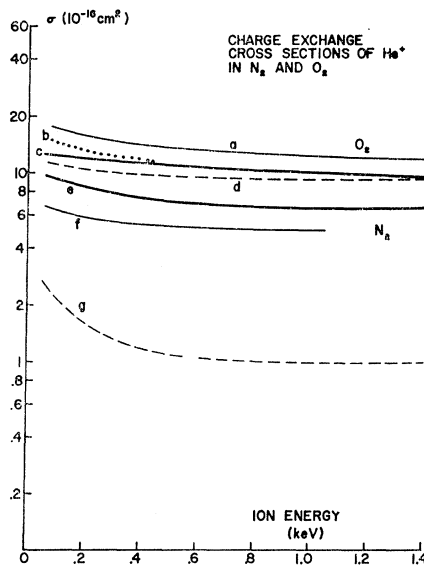

FIG. 8. Charge-exchange cross sections for He^+ ions in nitrogen and oxygen. Solid curve c, present results for O_2; a, Fite *et al.* (Ref. 8); b, Stebbings *et al.* (Ref. 10). Solid curve e, present results for N_2; d, Stebbings *et al.* (Ref. 10); f, Wolf (Ref. 4); g, Gustaffson and Lindholm (Ref. 6).

an energy defect would account for the decrease of the cross section below 800 eV. The general shape of the cross-section curve is similar to that observed for the $H^+ + Ar$ process reported in I and in Ref. 14, where $|\Delta E| \simeq 2.2$ eV.

For the $H_2^+ + N_2$ process a cross section was measured similar in form (but about 20% higher) than that obtained in Ref. 6, where the process $H_2^+ + N_2 \rightarrow H_2 + N_2^+$ was found to be most important. The relatively flat cross-section energy dependence, with an increase below 200 eV, suggests a near-resonance process. Ionization of H_2 to the H_2^+ ground state ($^2\Sigma_g^+$) requires 15.44 eV and Franck-Condon arguments indicate the electronically excited states of H_2^+ with energies between 16.4 and 17.1 eV may be preferentially excited and present in the beam ions; N_2^+ may be formed in the $X^2\Sigma_g^+$ (15.58 eV) or $A^2\Pi_u$ (16.69 eV) states. Therefore, there are opportunities for near-resonant charge transfers which when coupled with polarization interactions can yield large cross sections at low incident energies.

For $He^+ + N_2$ collisions, Ref. 6 has shown the process $He^+ + N_2 \rightarrow He + N^+(^3P) + N(^4S)$ would account for the observed predominance of N^+ in the collected products and yield $|\Delta E| \simeq 0.28$ eV, thus explaining the weak energy dependence. Note, however, that the charge-exchange cross sections for this process measured in the present work are about a factor of 6 larger than these reported in Ref. 6 and about 60% larger than the older measurements of Wolf.[5] This discrepancy is probably explained by the fact that the N^+ ion is formed with a kinetic energy of a few eV; the "weak" electric field that collected ions in Gustaffson and Lindholm's work was initially tested on exact resonance rare-gas collisions and appears to have been too feeble to capture a large fraction of the N^+ ions. Because it is not likely that the collection efficiency would be greater than unity, it appears that the present values are more nearly correct. Collection studies, of the type portrayed in Figs. 4 and 5, confirm that the product ions had energies of several eV; the cross section given may require an upward adjustment, particularly at the lower-energy

FIG. 9. Charge-exchange cross sections for water vapor. Solid curves, present results for H^+ and He^+; dashed curve, present results for H_2^+; closed circle and triangle, results for H^+ and H_2^+, respectively, Cable (Ref. 17).

end, where data were taken at weaker collection fields to avoid distortion of the incident ion beam.

Water Vapor

The results obtained for H_2O and CO_2 are difficult to interpret because of the imperfect understanding of the molecular structure of the H_2O^+ and CO_2^+ species. The polyatomic structure of the target molecules allows a wider range of internal excitations and a more complex dissociation pattern. The reaction $H_2^+ + H_2O$ is the only process which does not clearly have an increasing cross section below 100 eV. This is somewhat surprising,

because electron-impact studies on H_2O have yielded values for the appearance potentials of H_2O^+ ions of 12.6 eV, corresponding to the ground $^2B_1$ state, as well as at 14.35 and 16.34 eV, corresponding to the $^2A_1$ and $^2B_2$ excited states, respectively.[14-16] As noted above, unexcited ground-state H_2^+ ions have a 15.44-eV reappearance potential, and there is evidence to suggest that the ions are frequently formed with reappearance potentials in the 16–17 eV range. It would seem, therefore, that there would be an opportunity for the near-resonant collisions to yield increasing cross sections down to the lowest energies examined. Such behavior does seem to occur for the $H^+ + H_2O$ process, as well as for the $He^+ + H_2O$ process where resonance cannot be explained without invoking highly excited states of H_2O^+.

Also shown in Fig. 9 are data points obtained by Cable[17] for charge exchange of H^+ and H_2^+ on water vapor. Note that the relative magnitude and form of his values agree with the present work. That experiment was done using crossed beams and relative detectors which were only approximately calibrated, so that the absolute disagreement by practically one order of magnitude is probably not significant. In Cable's work, the charge-exchange products for the process $H^+ + H_2O$ were analyzed by energy and angle but not by species. It was found that the products left the interaction region with energies ranging from zero to a few volts, the more energetic products tending to emerge at angles about 20° forward of perpendicular.

The collection characteristics for the products of the $H^+ + H_2O$ interaction are shown in Fig. 4. Note that fields of about 4 V/cm are adequate to saturate the net collected current. Because the Cable data show that
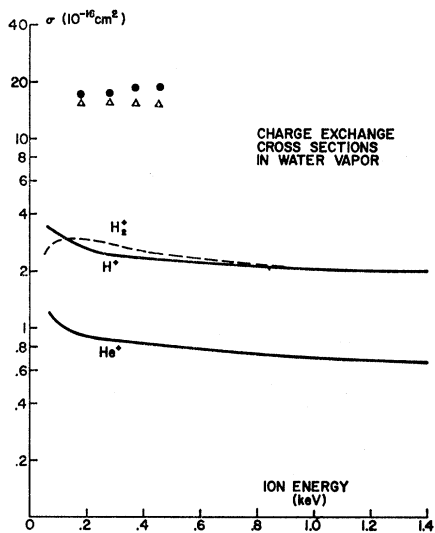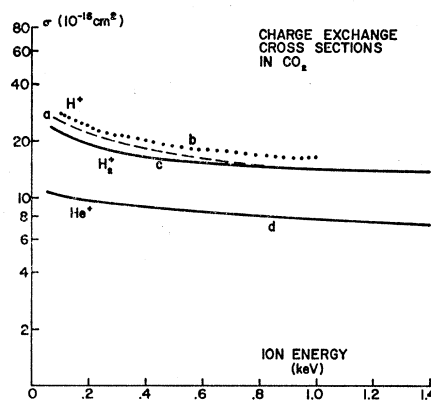

FIG. 10. Charge-exchange cross sections in CO_2. Solid curves c and d, present results for H_2^+ and He^+; dashed curve a, present results for H^+; dotted curve b, unpublished results for H^+ obtained by the author using the collision chamber from paper I.

[14] D. C. Frost and C. A. McDowell, Can. J. Chem. **36**, 39 (1958).
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[16] M. M. Mann, A. Hustrulid, and J. T. Tate, Phys. Rev. **58**, 340 (1940).
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products with energies up to 4 eV are characteristic of this reaction, a rule of thumb for the particular collection geometry employed in the present work might be that the collection field should be about equal to the maximum particle energy for satisfactory collection.

Collection data for the $He^+ + H_2O$ process show that about 9 V/cm is adequate to collect all collision products, indicating that the bulk of the charged products have energies below 10 eV. In view of the large energy defects between the reacting species and the resonant-like form of the cross section, this would suggest that the charged products for that reaction could be heavy fragments (i.e., OH^+ or O^+) of the H_2O^+ ion temporarily formed by charge exchange.

Carbon Dioxide

The results obtained for charge exchange in CO_2, shown in Fig. 10, also include data obtained with the old collision chamber that was used for the measurements reported in I. Note that the two measurements agree to within $\pm 10\%$, showing that the results reported in that paper were probably accurate and were not influenced by shortcomings in the earlier collection-system design. The CO_2^+ ion has an appearance potential for the $X^2\Pi_g$ ground state of 13.8 eV, and excited states appearing at 16.8, 17.4, and 19.4 eV, relative to the neutral molecular ground state.[18] Hence close resonance for collisions with H^+ or H_2^+ is expected, although higher excited states, repulsive states, or coupling with internal degrees of freedom[19] must be invoked to explain the form of the $He^+ + CO_2$ curve. The collection current versus collection field data for this reaction show that fields of 7 V/cm are required to collect the collision products, suggesting that products with energies in the 5–7 eV range are formed, perhaps through dissociation of excited CO_2^+.

CONCLUSIONS

The charge-exchange cross sections measured in this investigation are generally characterized by little energy dependence down to 40 eV, with the exceptions of the $H^+ + N_2$ and $H^+ + O_2$ reactions, which can be understood by applying adiabatic-theory criteria to the ground states of the species involved. Most of the other processes require that excited molecular states be invoked to yield the small values for $|\Delta E|$ (< 1 eV) that are appropriate to explain the observed results in terms of the adiabatic theory. The experimental evidence that the processes $He^+ + N_2$ and $He^+ + O_2$ yield energetic products, when coupled to previous determinations of dissociated products for these reactions, appears to confirm that charge exchange to unstable excited states dominates these reactions. For the other collision processes, the contributions of excited states are more difficult to assess. A recent study of optical excitation by ion impact on molecular gases has indicated that excited states of both the incident and target species can result from collisions at energies of less than 2 keV, where charge exchange is likely to be the dominant reaction.[20]

Further experimental studies of charge-exchange processes involving molecular species would be most valuable if they incorporated as many provisions as possible for examining the detailed features of the reaction. The mass, energy, and angular distribution of the products, together with energy and angular spread of the fast neutralized species should be measured and related to the energy defects through the kinetic conservation laws.[21] Spectroscopic observations of emitted radiation and detection of possible metastable products should also be incorporated in future studies to give a more complete description of charge-exchange processes.

ACKNOWLEDGMENTS

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