Retarding-Potential Measurement of the Kinetic Energy of Electrons Released in Penning Ionization*

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Kinetic energy of electrons released in ionization of N2, CO, NO, COS, CO2, C2H2, CH4, C2H6, C3H8, and $n-C_4H_{10}$ by means of helium atoms in metastable 2^1S and 2^3S states was measured and the energy of electronically excited ionic states determined. In N2, CO, COS, and CO2 all accessible excited states were populated probably by a Franck-Condon transition. Ionization of NO seems to proceed through pre-ionization of the HeNO complex in which a part of internal energy is converted into kinetic energy of He and NO+. In ionization of C_2H_2 and CH_4 , energy which can be effectively stored in the $C_2H_2^+$ and CH_4^+ ions in the ground state was determined and the aspects of the dissociative ionization discussed. In ionization of C_2H_6 , C₃H₈, and *n*-C₄H₁₀, more excitation energy is conferred on the ions than in ionization by charge transfer or electron impact.

INTRODUCTION

N the studies of ionizing collisions, increasing atten-L tion has been paid recently to ionizing collisions of excited neutral particles with atoms and molecules at thermal energy (ionizing collisions of the second kind or Penning ionization).¹⁻⁴ These studies are important from several points of view:

(1) Penning ionization differs from that caused by electron and photon impact or charge transfer, as the collisions occur between uncharged particles and the force field is small unless the particles are very close together.

(2) The collision time is increased and the collision may have adiabatic character. Collision complexes as an intermediate step may be favored. If the complexes survive some vibrations, the Franck-Condon principle may not be applicable in predicting the population of excited levels in the ions formed.

(3) Because the population of various electronically and vibrationally excited states of polyatomic ions may differ from that attainable through ionization by charged particles or photons, the influence of initial preparation of the ions on their subsequent dissociation may be investigated.

(4) Only one electron is released in ionization. In measuring its kinetic energy, data related directly to the energy of excited states of ions are accessible. Especially, data on the distribution of excitation energy in polyatomic ions are obtainable in a straightforward way.

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¹W. P. Sholette and E. E. Muschlitz, Jr., J. Chem. Phys. 36, 3368 (1962).

² E. E. Fergusson, Phys. Rev. 128, 210 (1962).

³ E. E. Muschlitz, Jr., and M. J. Weiss, *Atomic Collision Pro-*cesses, M. R. C. McDowell, Ed. (North-Holland Publ. Co., Amsterdam, 1964), p. 1073.

V. Čermák and Z. Herman, Collection Czech. Chem. Commun. 30, 169 (1965).

This is important for the theories of dissociative ionization of molecules.⁵

(5) The determination of kinetic energy of electrons released in associative ionization may be used, in favorable cases, to estimate the binding energy of complex ions produced.6

Studies have been undertaken already to determine the kinetic energy of electrons released in photoionization,7-15 but no work has dealt with such measurement in Penning ionization. It is clear that once the data about this process become available, comparative studies of all kinds of ionization of simple as well as polyatomic molecules would be of great importance.

This paper is closely related to a study published previously on Penning ionization of polyatomic molecules.⁴ An independent measurement of kinetic energy of electrons released was desirable for verifying the conclusions made. The work reported here is limited to the ionization of N2, CO, NO, COS, CO2, C2H2, and CH4 by means of excited helium atoms in the $2^{1}S$ and $2^{3}S$ metastable states.

⁶ H. M. Rosenstock and M. Kraus, *Mass Spectrometry of Organic Ions*, F. W. McLafferty, Ed. (Academic Press Inc., New York, 1963).

¹⁹⁰³).
⁶ Z. Herman and V. Čermák, Nature **199**, 588 (1963).
⁷ B. L. Kurbatov, F. I. Vilesov, and A. N. Terenin, Soviet Phys.—Doklady **6**, 490 (1961); **6**, 883 (1962) [Dokl. Akad. Nauk SSSR **138**, 1329 (1961); **140**, 797 (1961)].
⁸ F. I. Vilesov and B. L. Kurbatov, Izv. Akad. Nauk SSSR, Ser. Fiz. **27**, 1088 (1963).

⁹ F. I. Vilesov, Usp. Fiz. Nauk **81**, 669 (1963) [English transl.: Soviet Phys.—Usp. **6**, 888 (1964)].

¹⁰ D. W. Turner and M. I. Al-Johoury, J. Chem. Soc. (London) 1963, 5141.

¹¹ D. W. Turner and M. I. Al-Joboury, J. Chem. Phys. 37,

3007 (1962). ¹² M. I. Al-Joboury and D. W. Turner, J. Chem. Soc. (London) 1964, 4434. ¹³ R. I. Schoen, J. Chem. Phys. 40, 1830 (1964) ¹³ R. I. Schoen, Paper RB

⁴ P. H. Doolitile and R. I. Schoen, Paper RB-I presented at the Proc. Intern. Conf. Phys. Electron. At. Collisions 4th Quebec,

¹⁵ D. C. Frost, C. Λ. McDowell, and D. Λ. Vroom, Paper RΛ-5, Ref. 14.

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EXPERIMENTAL

The apparatus used was described in a previous publication.¹⁶ The molecular gases were admitted into the collision region through a variable leak. They were of the Matheson C.P.-grade quality and were stored in the commercial lecture bottles. The pressure inside the collision region was of the order of 5×10^{-4} - 10^{-3} mm Hg.

Data were obtained in the form of the integral stopping-potential curves which show the dependence of the current of electrons reaching the collector on the potential difference applied between the grid and the cylinder. A derivative of the stopping-potential curve was then constructed as $\Delta i / \Delta V$, $\Delta V = 0.1$ V. Because of field penetration and contact potentials, the actual electron energy, and hence the excitation of the ions, had to be obtained by calibration of the stoppingpotential scale. For this purpose argon was used. Electrons released in its ionization by helium atoms in the $2^{1}S$ state have the energies of 20.61-15.76=4.85eV and 20.61 - 15.94 = 4.67 eV, and those released in ionization by the 2³S state have the energies 19.81-15.76=4.08 eV and 19.81-15.94=3.87 eV. In the arrangement used, the electron-energy resolution was about 22 (see Ref. 16). It is not enough to separate the steps due to argon-ion doublets ${}^{2}P_{\frac{1}{2}}$ and ${}^{2}P_{\frac{1}{2}}$ so that only two steps appear on the integral curve instead of four. The corrected stopping-voltage scale was shifted to lower voltage by about 0.7 eV. Steps on the integral curve were identified as belonging to ionization into the ground state of the ions by means of calibration. The onset of the first step (ionization by $2^{1}S$ helium atoms) was used as the zero point on the excitation energy scale. The zero point on the excitation energy scale for ionization with helium atoms in the 23S state is obtained by shifting the zero point to the left by 0.8 eV.

The accuracy of determining the energy values depended on the peak shape and was lowered by considerable background due to scattered electrons. It was about ± 0.1 eV. No conclusions were made from peak heights on the relative excitation cross sections because the collection efficiency for electrons with different energy was not tested.

RESULTS AND DISCUSSION

Nitrogen

The integral stopping-potential curve and its derivative are shown in Fig. 1. In spite of considerable background, the formation of N_2^+ ions in the ground state and in two excited states is clearly detected (Peaks 1–3, Curve 2). Peaks 1a, 2a, and 3a are due to ionization by the 2¹S atoms and Peaks 1b, 2b, and 3b by the 2³S atoms. Their separation at the onset of the steps is 0.8 eV which is the energy difference of the two states (20.61–19.81 eV). Peaks 1, 2, and 3 correspond to the following processes:

$$\operatorname{He}^{*}(2^{1}S, 2^{3}S) + \operatorname{N}_{2} \rightarrow \operatorname{N}_{2}^{+}(A^{2}\Pi_{u}) + \operatorname{He}(1^{1}S) + e. \quad (1)$$
$$\searrow_{\operatorname{N}_{2}^{+}(B^{2}\Sigma_{g}^{+})}$$

The onsets of Peaks 2b and 3b are separated from the onset of Peak 1b by 1.1 and 3.3 V, respectively. These energies are close to the $A \,{}^{2}\Pi_{u} - X \,{}^{2}\Sigma_{g}^{+}$ and $B \,{}^{2}\Sigma_{g}^{+} - X \,{}^{2}\Sigma_{g}^{+}$ separations, the spectroscopic values of which are,^{17,18} respectively, 1.1 and 3.15 eV.

The peaks of the ground state and of the $B \,{}^{2}\Sigma_{g}^{+}$ state are narrower than the peak of the $A \,{}^{2}\Pi_{u}$ state as if only few vibrational levels were excited in the ground and the $B \,{}^{2}\Sigma_{g}^{+}$ states. This is in agreement with the shape of the potential-energy curves for the three states in question. The internuclear separation in the $A \,{}^{2}\Pi_{u}$ state, 1.190 Å, is larger than in the neutral $X \,{}^{1}\Sigma_{g}^{+}$ state, 1.094 Å; whereas the $X \,{}^{2}\Sigma_{g}^{+}$ and the $B \,{}^{2}\Sigma_{g}^{-}$ states have equilibrium separations close to the neutral ground state (1.116 and 1.075 Å, respectively).¹⁸ Higher vibrational levels are, therefore, excited in the $A \,{}^{2}\Pi_{u}$ state; and the Peaks 2a and 2b spread to lower electron energies.

Carbon Monoxide

The integral and differential curves are shown in Fig. 2. Peaks 1a and 1b correspond to CO⁺ ions formed in the ground state. Peak 3a is due to the process

$\operatorname{He}^{*}(2^{!}S) + \operatorname{CO} \rightarrow \operatorname{CO}^{+}(B^{2}\Sigma_{\varrho}) + \operatorname{He}(1^{!}S) + e. \quad (2)$



FIG. 1. Dependence of the electron current to the collector on the stopping potential for N₂. (I.P. N₂=15.6 V.) Curve 1: integral curve. Curve 2: differential curve. Peaks 1, 2, and 3 refer to the ground, first, and second excited states of N₂⁺ ion, respectively. The letter "a" denotes ionization by 2¹S atoms, "b" denotes ionization by 2³S atoms.

¹⁶ V. Čermák, J. Chem. Phys. 44, 3774 (1966).

¹⁷ F. R. Gilmore, Memorandum RM-4034-PR, The Rand Corp., Santa Monica, Calif., June 1964.

¹⁸ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1950).

The spectroscopically determined energy of the $B \,^2\Sigma_a$ state is 5.86 eV above the CO⁺ ground state, and the measured difference of the stopping potentials at the onset of the Peaks 1a and 3a is 5.6 eV. The very small and broad peak 2b in the region of uncorrected stopping potential (near 3.3 V) is due to the ionization to the first excited state of CO⁺, $A \,^2$ II, by helium atoms in the 2^3S state. The peak belonging to the ionization by the 2^1S atoms is too small to be seen.

Nitric Oxide

Figure 3 shows that there are no pronounced steps or breaks on the integral curve at stopping potentials larger than 5 V which would belong to the first or second ionization potentials of NO (9.24 and 14.2 V).¹⁷ Therefore, instead of using a calibrated excitation energy scale, the energy is given in ionization potentials



FIG. 2. Integral and differential stopping-potential curves for CO. (I.P. CO = 14.01 V.) The same notation is used as in Fig. 1.

corresponding to the onsets of the steps on the integral curve caused by the $2^{1}S$ atoms.

Ionization by both $2^{1}S$ and $2^{3}S$ atoms is clearly detectable at 16.3 and 17.1 V. The value of 16.3 V is very close to the ionization potential of the $^{3}\Delta$ state at 16.55 V.¹⁷ The broad peak with the maximum at about 19.5 V belongs probably to ionizations to the Λ ¹II, $^{3}\Sigma^{-}$ and $^{1}\Sigma^{-}$ states lying in the region of about 18.5 V.¹⁷

The absence of the steps for the NO⁺ ions in the ${}^{1}\Sigma^{+}$ ground state and in the $A {}^{3}\Sigma^{+}$ first excited state is striking in comparison with the results in N₂ and CO where the Franck–Condon transitions seem to occur. It is probable that a collision complex HeNO is formed and that pre-ionization of the complex determines the population of various excited states of NO⁺ ions. If this occurs, the energy of electrons released will be indicative of the energy states of NO⁺ ions only when no transformation of internal energy of the complex HeNO into kinetic energy of He and NO⁺ takes place. Such



FIG. 3. Integral and differential stopping-potential curves for NO. (I.P. NO=9.24 V.)

transformation could account for the broad peak on the differential curve at about 10.5-12 V. This peak would then correspond to ionization of NO and to the formation of NO⁺ ions in the ground state in a process in which He and NO⁺ ions acquire together a kinetic energy of about 1.3 eV.

Carbonyl Sulfide

The integral and differential curves shown in Fig. 4 reveal quite clearly the ionization by both 2^1S and 2^3S atoms into the COS⁺ ionic ground state (Peaks 1a, 1b) and into the first and second excited states (Peaks 2 and 3). The excitation energy of the first excited state is 4.8 eV, and that of the second excited state is 6.8 eV. These values compare well with the spectroscopic values of 4.74 and 6.64 eV.¹⁹

Carbon Dioxide

According to the integral and differential curves shown in Fig. 5, the CO_2^+ ions are formed, not only in



FIG. 4. Integral and differential stopping-potential curves for COS. (I.P. COS=11.3 V.)

¹⁹ Y. Tanaka, A. S. Jursa, and F. J. LeBlanc, J. Chem. Phys. 28, 350 (1958).



FIG. 5. Integral and differential stopping-potential curves for CO₂. (I.P. $CO_2 = 13.8 \text{ V.}$)

the ground state (Peaks 1a, 1b), but in three excited states lying 3.6, 4.2, and 5.6 eV above the ground state of CO_2^+ ions (Peaks 2, 3, and 4). Accidentally, peak 2b, which results from ionization by the 2³S atoms and from the formation of the CO_2^+ ions in the first excited state, coincides with Peak 3a due to the ionization by 2¹S atoms into the CO_2^+ second ionic excited state. The spectroscopically determined excited states of CO_2^+ ions have the energies of 3.5, 4.24, and 5.51 eV above the CO_2^+ ion ground state (I.P.=13.78 V).¹²

Acetylene

The integral stopping-potential curve (Fig. 6, Curve 1) differs from those for N_2 , CO, NO, COS, and CO₂ in two respects: the steps on the curve become asymmetrical, and the first step is relatively smaller. The tailing, well marked on Peak 1b (Fig. 6, Curve 2), is due to the vibrational excitation of the $C_2H_2^+$ ion and to the decreasing transition probability of excitation of higher vibrational levels. The width at the bottom of peak 1B is about 2.5 eV. A value of 1.8 eV is obtained for the maximum vibrational energy which can be effectively stored in the $C_2H_2^+$ ion if one subtracts 0.7 eV (peak width for argon, see Ref. 16) to correct for the peak width caused by the incomplete energy resolution. More vibrational excitation is still possible, but the transition factors become very small.

The relatively small cross section for ionization by the $2^{1}S$ atoms is surprising. It was checked by changing the current of exciting electrons so that it is not due to an unexpected quenching of the $2^{1}S$ state in the source by secondary electrons. A tentative explanation might be that an important part of the ionization of $C_{2}H_{2}$ occurs in two steps, the first being the formation of a superexcited molecule in a triplet state:

$$He^{*}(2^{3}S) + C_{2}H_{2}({}^{1}\Sigma_{g}^{+}) \to C_{2}H_{2}^{**}({}^{3}) + He(1^{1}S), \qquad (3)$$

and the second step the pre-ionization of the excited molecule:

$$C_2H_2^{**} \rightarrow C_2H_2^+ + e. \tag{4}$$

Total spin is conserved in Reaction (3), but spin would be changed if atoms in the $2^{1}S$ state reacted. The $2^{1}S$ state can, of course, react according to

$$\operatorname{He}^{*}(2^{1}S, 2^{3}S) + C_{2}H_{2} \rightarrow C_{2}H_{2}^{+}(^{2}) + \operatorname{He}(1^{1}S) + e.$$
 (5)

Reaction (5) with $2^{1}S$ atoms then accounts for the first step on the curve.

The kink on Curve 1 or the broad peak at 3–4.5 V on Curve 2 in Fig. 6 could be explained by assuming that it manifests a second ionization potential of C_2H_2 lying 5.1 eV above the first. The ionization potential of C_2H_2 of 16.27 V was reported by Al-Joboury *et al.*²⁰ The value I.P. = 15.5 V for the ionization potential into the first excited state of $C_2H_2^+$ ions, obtained by Lindholm and Szabo³¹ in charge-transfer experiments, is lower but the right value is probably about 16.5 V.²²

Similarly, the rise on the differential curve at the stopping potential of about 2.6 V might reveal an excited state of $C_2H_2^+$ ions having an energy higher than 7.0 eV. An excited state found earlier in photoionization studies lies 6.95 eV above the ground state.¹²

It is important to note that valuable conclusions on the mechanism of dissociative ionization of C_2H_2 can be made from the shape of the electron-energy distribution curve. In ionization of C_2H_2 electrons with kinetic energy of 20.6-17.8=2.8 eV and 19.8-17.8=2.0 eV (17.8 V is the appearance potential of C_2H^+ ions from C_2H_2)²² corresponding to the dissociative ioni-



FIG. 6. Integral and differential stopping-potential curves for $C_2H_2.$ (I.P. $C_2H_2{=}11.41$ V.)

²⁰ M. I. Al-Joboury, D. P. May, and D. W. Turner, J. Chem. Soc. (London) **1965**, 616.

²¹ E. Lindholm, I. Szabo, and P. Wilmenius, Arkiv Fysik 25, 417 (1963).
²² E. Lindholm (private communication to the author).

zation, well known from electron-impact studies,

$$C_2H_2^+ \longrightarrow C_2H^+ + H \tag{6}$$

could appear as a separate peak on the energy distribution curve. This would be the case if the dissociation occurred from a repulsive state. There is no indication of a peak in the region mentioned. Thus, it can be concluded that either the C₂H₂⁺ ions dissociate from sufficiently high vibrational levels of the first electronically excited state or that the repulsive curve has a shape leading to a large energy spread of electrons released which makes these electrons undetectable in present experiments. It is also possible that ionization and dissociation proceed via a pre-ionizing superexcited state which can be formed in electron impact but which is not accessible in collisions with excited neutral atoms. However, the fact that $C_2H_2^+$ ions appear in the mass spectrum of C_2H_2 ionized by metastable helium atoms⁴ indicates that the most plausible mechanism of the formation of C_2H^+ ions in Penning ionization is the dissociation from the first electronically excited state of $C_2H_2^+$ ions. These questions could be answered by using an apparatus with sufficiently high energy resolution.

Methane

The integral curve (Fig. 7) is **S** shaped with long tailing and without prominent separation into two steps. The two groups of electrons with energies 20.61 - 12.98 = 7.63 eV and 19.81 - 12.98 = 6.53 eV are poorly discernible even on the differential curve. The electronenergy distribution peaks are broader because of more vibrational excitation in the CH₄+ ion. The total width of the peaks on Curve 2 in Fig. 7 is 4.4 eV. Subtracting 0.8 eV (energy difference of the 2^1S and 2^3S states) and 0.7 eV (peak broadening at the bottom due to im-







FIG. 8. Dependence of the electron current to the collector on the stopping potential for C_2H_6 (Curve 1), C_3H_6 (Curve 2), and n- C_4H_{10} (Curve 3). Curve 1b is the differential of the Curve 1a. A tentative location of the onsets on Curve 1b is marked with arrows.

perfect energy resolution), a value of 2.9 eV is obtained for the maximum energy which can be effectively accomodated in the CH_4^+ ion. Higher vibrational excitation is still possible, but the transition probabilities become very small.

The maximum on the differential curve (Fig. 7) is not located close to the zero excitation energy but is shifted to greater energies. This result and the tailing at the bottom of the peaks seem to indicate that the difference in geometry and frequencies of the CH_4^+ ion and CH_4 molecule are reflected in the transition probabilities in Penning ionization in a similar manner as in photoionization.²³

There is no indication, within the limits of the sensitivity of the apparatus, of a second ionization potential in the range of 13-19 V. The dissociative ionization of CH₄ to CH₃⁺ and to CH₂⁺ ions at the potentials of 14.25 and 15.16 V,²⁴ respectively, remains undetected in Penning ionization. This means that it occurs from vibrationally excited CH₄⁺ ions in the ground state because pre-ionizing states lying at the appearance potentials of CH₃⁺ and CH₂⁺ ions are not formed in impact with metastable atoms of helium.

Ethane, Propane, and *n*-Butane

The integral curves for all three gases and the differential curve for ethane are shown in Fig. 8. Tailing of the steps becomes more pronounced when going from C_2H_6 to n- C_4H_{10} , and the structure gradually disappears. Evidently, ionization by both 2^1S and 2^3S atoms prevents any conclusions other than general ones to be made.

 ²³ V. H. Dibeler, M. Kraus, R. M. Reese, and F. N. Harlee, J. Chem. Phys. 42, 3791 (1965).
 ²⁴ H. von Koch, Arkiv Fysik 28, 529 (1965).

In ethane the enhanced probability of excitation of $C_2H_6^+$ ions at 4–6.5 V (Fig. 8, Curve 1b) suggests that minimally one electronically excited state exists. From the onsets on the electron-energy distribution curve, one can estimate roughly that its energy lies about 3.7 eV above the $C_2H_6^+$ ion ground state. The accurate value reported earlier is 3.24 eV.¹²

The excitation energy distribution curves for $C_2H_6^+$ and $C_3H_8^+$ ions, the only ones which can be determined from the integral curves in Fig. 8, differ substantially from those obtained by von Koch in a charge-transfer study of C₂H₆²⁵ and by Chupka in an electron-impact investigation of C_3H_8 .²⁶ For $C_2H_6^+$ ions the probability of excitation should be at a maximum at 1-1.5 eV excitation energy.²⁵ However, in experiments presented here the broad peak appears at about 5 eV. The situation is similar for $C_3H_8^+$ ions.²⁶ This means that in Penning ionization more excitation energy is accommodated in the $C_2H_6^+$, $C_3H_8^+$, and probably also in $n-C_4H_{10}^+$ ions than in ionization by charge transfer or electron impact. These direct experimental results thus verify the same conclusions made previously in an indirect way.4

CONCLUSIONS

The data obtained in measuring kinetic energy of electrons released in Penning ionization and pertaining to the location of electronically excited ionic states exhibit some similarities and differences with respect to photoionization.

Ionization by helium metastable atoms of N₂, CO, COS, and CO₂ occurs probably in a Franck-Condon

 ²⁵ H. von Koch, Arkiv Fysik 28, 559 (1965).
 ²⁶ W. A. Chupka and M. Kaminski, J. Chem. Phys. 35, 1991 (1961).

transition with the populating of all energetically accessible spectroscopically known ionic states.

Ionization of NO seems to proceed through preionization of an HeNO complex, as some electronically excited states of NO+ ions are not populated. When the HeNO complex pre-ionizes, a part of its internal energy is probably converted into kinetic energy of both He and NO⁺ ions.

The shape of the electron-energy distribution curve in ionization of acetylene and methane indicates that the transition factors for conferring more excitation energy than about 1.8 eV to the $C_2H_2^+$ ion and about 2.9 eV to the CH_4^+ ion become very small. The latter result compares well with the value obtained in chargetransfer studies. However, the excitation energy accommodated in $C_2H_6^+$, $C_3H_8^+$, and $n-C_4H_{10}^+$ ions in Penning ionization is greater than in either charge transfer or electron-impact ionization.

The type of apparatus used did not allow either for determination of the population of vibrational levels of various electronically excited states or for precise measurement of the ionization potentials. In future studies use will be made of the electrostatic electron energy analyzer and of ionization with a beam of helium atoms of one kind only. Promising data could then be obtained on the mechanism of dissociative ionization as well.

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