

MEAN MOMENTUM AND EXCITATION ENERGY OF ARGON IONS

L. V. SUMIN, M. V. GUR'EV, and N. N. TUNITSKIĬ

L. Ya. Karpov Physico-chemical Institute

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A method for determining the excitation energy of molecular ions is described, based on measurement of the momentum transferred to the atom or molecule by the electron.

Experimental values of the momenta of a number of ions and the respective values of their excitation energies are presented. The mean energy transferred to an atom by the ionizing electron was found to be surprisingly high for Ar^+ ions, about 50 eV.

IONIZATION by a fast electron produces a positive ion having a certain momentum. Starting from the conservation laws, we can relate this momentum with the energy transferred by the electron to the atom or to the molecule and lost to ionization and excitation. It is necessary to use here the data on the energy and angular distributions of both secondary electrons.

From the conservation laws we have for ionizing electrons of energy E_0 and momentum p_0

$$2p_2^2 + p^2 + 2p_2p - 2p_0(p_2 + p) + 2mJ = 0, \quad (1)$$

where m —electron mass, p_2 —momentum of slow electron, p —momentum of ion, J —sum of the excitation energy and the ionization potential.

We know that at sufficiently large values of E_0 , one of the two secondary electrons is faster and is emitted in a direction close to that of the incoming electron, while the second electron is slow, with energy on the order of 1–3 eV. The slow electrons have an approximately isotropic angular distribution^[1].

In this connection we can assume that averaging yields $\bar{p}_2 = 0$ and low values for \bar{p}_2^2 and \bar{p}^2 . We can then obtain J from (1), using the experimentally determined value of \bar{p}_x —the average projection of the ion momentum on the p_0 direction.

At low primary-electron energies E_0 (on the order of the ionization potential of the atom or the molecule) each secondary electron has an energy of several electron volts and both have an isotropic distribution^[1,2]. In this case the average ion momentum will be close to that of the incoming electron (see the momentum of He^+ for $E_0 = 30$ eV in the table). By averaging (1) over the secondary-electron energy and angular distributions given by the simplest collision theory of Thomson^[3], we obtain for $E_0 \gg J$

$$\bar{p}_x = 0.85J\sqrt{m/E_0}. \quad (2)$$

From a comparison of (1) and (2) we see that, under the simplifications made in formula (1), the results obtained practically coincide. This means that, for given values of J and E_0 , the details of the angular distribution of the secondary electrons have little effect on the magnitude of the momentum transfer.

By measuring the velocity acquired by the atomic or molecular ion we can thus determine the energy lost by the electron to excitation and ionization of the atom or the molecule. The velocity of the positive ions was measured with a mass spectrometer by a deflection method^[4] consisting in registering the distribution of the ions over the velocity projections on a selected direction, in this case on the direction of the primary electron beam. The momentum transferred by the electron upon ionization is manifest essentially in a shift of the distribution function of the ion-velocity projections on the direction of the electron impact. In practice one records the relative shift of the distributions over the velocity projections for different ions from a mixture of two gases. The larger the mass difference of the mixture components, the more accurate the measurement of the momentum of the lighter ions and the less stringent the requirement on the accuracy with which the momentum of the heavy ions is estimated by means of formula (2). As a rule the heavy ions of molecular N-hexane are used. The correction for the momentum of this ion amounts to not more than 20% of the measured value. The main results are listed in the table. The third column of the table shows the experimentally measured average momentum projections, i.e., the square roots of the corresponding energies.

Ion	Electron energy E_0 , eV	$\bar{p}_x \cdot 10^3$, eV ^{1/2}	J , eV
Ar ⁺	180	9.5±1	56±6
He ⁺	30	52±6	—
He ⁺	140	20±3	33±5
H ₂ ⁺	180	13±2	17.4±3
CH ₄ ⁺	90	4±2	10±5
C ₃ H ₈ ⁺	140	2±2	11±11

The excitation energies calculated from (2) are listed in the fourth column of the table. The data obtained show that the fraction of the excited He⁺ ions is small and does not exceed 10–15 per cent of the total number. The unexpected large value of the argon-ion excitation cannot be completely attributed to inaccuracies in the calculation, since the angular distribution of the secondary electrons has the usual character for argon^[5], and the obtained momentum value in the absence of ion excitation calls for the faster of the secondary electrons to be scattered, in the mean, at an angle of 40° to the primary beam direction. Although the accuracy of calculation by formula (2) does not make it possible to establish reliably the excess of the energy above the potential for double ionization of argon (43 eV), the data obtained offer definite evidence of the presence of large excitation of the Ar⁺ ions. The energy lost by the fast particle in the gas to the ion pair (28 eV^[6]) can be attributed to transfer of excitation energy from the ion to the other atom with ionization of the latter.

For the molecular ions H₂⁺, CH₄⁺, and C₃H₈⁺ the energy transfer is equal, within the limits of experimental error, to the ionization potential of these molecules. For H₂⁺ ions this equality is obligatory^[1].

The results obtained give only the energy transferred to the atom or to the molecule during

the collision, and no information on the lifetime of the excited state. It was recently shown that 10⁻⁵ sec after the collision some fraction of the Ar⁺ ions (approximately 1 per cent) still remains strongly excited^[7,8].

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