MEASUREMENTS OF THE CROSS SECTIONS FOR EXCITATION OF BANDS IN THE VISIBLE PORTION OF THE SPECTRUM OF CO *MOLECULES AND* CO^+ *IONS BY 0.4–20 KEV ELECTRONS*

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We have measured the cross sections σ for excitation by electron impact (E = 4 keV) of 14 bands of the CO^+ comet tail system (CO^+ c.t.s.), two bands of the CO^+ Baldet–Johnson system, and two bands of the CO molecule Angström system. In the electron energy range 0.4–20 keV we have measured excitation functions of the bands (2–0), (2–3), (3–0), (0–1), (1–0), and (1–1) of the comet tail system, the band (0–1) of the Baldet–Johnson system, and the band (1–0) of the Angström system. The experimental dependence $\sigma(E)$ is in good agreement with the functions calculated in the first Born approximation for all bands studied for energies $E > 0.4$ keV. We have calculated the dependence of the electronic transition moment R_e as a function of the internuclear distance r for the CO^+ c.t.s. on the basis of the experimental data. The $R_e(r)$ functions calculated in the present work and by Robinson and Nicholls[2] are in good agreement.

INTRODUCTION

SKUBENICH[1] has measured the cross sections and excitation functions of the bands of a number of systems of the CO molecule and the CO^+ ion in collisions of electrons with energies not greater than 150 eV with CO molecules. Robinson and Nicholls[2] have measured the relative intensities of the bands of the CO^+ ion comet tail system, also excited by slow electron impact. There is no information in the literature on the cross sections for excitation of these bands by fast electrons, although this information is of considerable interest for geophysics and astrophysics.

In order to fill this gap, we have measured in the present work the cross sections for excitation by fast electron impact of 14 bands of the comet tail system, the bands (0–0) and (0–1) of the Baldet–Johnson system of CO^+, and the bands (0–0) and (1–0) of the Angström system of the CO molecule. The experimental apparatus and the measurement technique have been described in detail previously,[3] and therefore we will dwell only briefly on some differences in technique between the present measurements and those reported in Ref. 3.

The excitation cross sections were calculated with the formula

$$\sigma_{i\lambda} = 0.9344\cdot 10^{-24} b_\lambda \epsilon_\lambda \frac{d\lambda}{dl}\frac{dl}{JP}\frac{N_{ig}}{N_{sl}}\ [\mathrm{cm}^2],$$

where b_λ is the spectral luminosity of a black body, ϵ_λ is the spectral emissivity of tungsten, $d\lambda/dl$ is the linear dispersion of the apparatus in Å/mm in the region $\lambda + \Delta\lambda$ for a given wavelength, dl is the spectrograph exit-slit width in millimeters, J is the current in μA, P is the gas pressure in mm Hg, and N_{ig} and N_{sl} are respectively the signals from the incandescent gas and from a standard lamp. The measurements were made in the single-collision region.

In measurement of the cross sections of the bands of the first negative system of N_2^+,[3] the spectral apparatus was adjusted so that the spectrograph exit slit accepted the radiation of the entire band being studied. The bands of the CO^+ c.t.s. have a strongly developed rotational structure. The total width of the bands of this system in our spectra was as high as 114 Å (the band (3–0)) or 3.0 mm in the linear dimension at the spectrograph exit. However, the maximum width of the entrance slit used in operation of the spectrograph was 1.5 mm, i.e., in some cases it did not permit the radiation of the entire band to reach the photomultiplier cathode. In these cases the cross sections were measured for the individual branches of the band, and the excitation cross section for the entire band was found by summation of these values.

In order to determine the necessary width of the exit slit, which was chosen to be not less than the width of the measured branch in the spectrum, a recording of the entire band was made on the tape of an ÉPP-09 recorder. The intensity of bands partially overlapped by other bands was measured with a branch which was free from superpositions. The total cross section for excitation of the band was calculated with allowance for the ratio of the band intensities, which were the same for all bands of this system.

In order to verify the correctness of the method used, we determined the absolute cross section for excitation of the band (2–3) in the CO^+ c.t.s. by two methods. Since the width of this band was no larger than the width of the spectrograph exit slit, it was possible to measure the total cross section of the band by a direct method. We also measured the cross section of only one branch, and the cross section of the entire band was calculated with allowance for the ratios of areas of the individual branches, as recorded on the recorder chart. The excitation cross sections measured in this way were consistent within the experimental errors. The statistical error of the measurements was ±10% for intense bands, and ±15% for weak bands.

The comet tail systems of CO^+

$v' - v''$	$\sigma \times 10^{-19}$, cm^2 (present work, E = 4 keV)	σ, rel. un. Present work, E = 4 keV	Ref. 1, E = 100 eV	Ref. 2, E = 100 eV	Calculation from the Franck-Condon factors
0—0	0,83	0.55	0.56	0.21	0,25
0—1	1.43	0,95	0.99	0.51	0.64
1—0	2.8	1.87	1.87	1,47	1.88
1—1	3.51	2,34	2.4	1,81	2.29
1—2	1.15	0.77	—	0.53	0,68
2—0	6.38	4,25	3.5	4.19	4.1
2—1	3.08	2.05	1.81	1.77	1,77
2—3	1,5	1	—	1	1
3—0	6,9	4.6	2.65	3.8	4.8
3—1	0,82	0.55	0.47	0,22	0.25
3—2	2,7	1.8	0.87	0,87	1,1
3—3	0.82	0.55	0.44	0.58	0.73
4—2	1.92	1,28	0.82	0.89	1.29
4—4	0.6	0.4	—	0,37	0.55

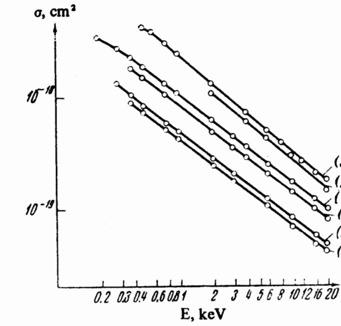

FIG. 1. Excitation functions for bands of the CO^+ comet tail system.

EXPERIMENTAL RESULTS AND DISCUSSION

1. The CO^+ Comet Tail System

For an electron energy of 4 keV we measured the excitation cross sections of the following bands of this system: (0–0), (0–1), (1–0), (1–1), (1–2), (2–0), (2–1), (2–3), (3–0), (3–1), (3–2), (3–3), (4–2), (4–4). The results obtained are given in the table. As can be seen from this table, the excitation cross sections of the measured bands vary from several units times 10^{-19} to several units times 10^{-20} cm^2. In view of the absence of data on the excitation cross sections of these bands when excited by fast electrons, the results of the present work can be compared only with relative values of the cross sections of the bands of the CO^+ comet tail system measured in the low-energy region.[1,2] The latter results are listed in columns 4 and 5 of the table. The data in columns 3 and 5 of the table have been normalized to the cross section of the (2–3) band of the CO^+ c.t.s. The cross sections listed in column 4 have been normalized to the cross section of the (1–0) band and are related by this band with the results of the present work. As can be seen from the table, the relative values of the cross sections of the CO^+ c.t.s. bands measured in Ref. 1 and calculated from the measured intensities of Ref. 2 for transitions from vibrational levels $v' = 1, 2, 3, 4$ of the state $A^2\Pi$ of the CO^+ ion are close to the relative cross-section values measured in the present work. An exception is the (3–2) band, for which σ in the present work is a factor of two larger than the value measured in Refs. 1 and 2. A possible explanation of this discrepancy may be the superposition on the CO^+ c.t.s. (3–2) band of the (0–1) band of the Angström system of the CO molecule.

The cross sections of bands formed in a transition from the zero vibrational level of the $A^2\Pi$ state differ somewhat in the measurements of various workers. Our data are in good agreement with the results of Robinson and Nicholls[2] but are higher than the values of σ obtained by Skubenich.[1] In the last column of the table we have listed the relative cross-section values calculated by means of the Franck–Condon factors. This calculation was carried out in the following way. The cross section of a certain band corresponding to the transition $(v' - v'')$ can be written in the form

$$\sigma_{v'v''} = A q_{v'} \nu^3_{v'v''} R_e^2(\bar{r}_{v'v''}) q_{v'v''}, \qquad (1)$$

where $q_{v'}$ is the Franck–Condon factor corresponding to a transition from the zero vibrational level of the ground state of the CO molecule to the vibrational level v' of the $A^2\Pi$ state of the CO^+ ion, $q_{v'v''}$ is the Franck–Condon factor for the radiative transition $(v' - v'')$, $\nu_{v'v''}$ is the wave number corresponding to the transition $v' - v''$, $R_e(\bar{r}_{v'v''})$ is the electronic transition moment, and A is a constant.

In the case where the electronic transition moment for the band system being studied depends weakly on the internuclear distance r, the transition probability $P_{v'v''} = R_e^2 q_{v'v''}$ is proportional to the Franck–Condon factor $P_{v'v''} \sim q_{v'v''}$. The relative cross sections were calculated from Eq. (1) with subsequent normalization to the (2–3) band. The calculation was made with $q_{v'v''}$ values from Nicholls[4] and $q_{v'}$ values from Wacks.[5]

As can be seen from the table, satisfactory agreement is observed for a number of bands between the cross-section values calculated from Eq. (1) and the measured values, although for some bands a substantial discrepancy is observed.

On the basis of the excitation cross sections measured in the present work for the bands of the CO^+ comet tail system, we calculated the function $R_e(r)$ by the same method used in Refs. 2 and 6. The analytic expression of this function is represented by the following formula:

$$R_e(r) = \mathrm{const} \cdot (-1 + 1.732r - 0.736r^2) \qquad (2)$$

for 1.13 Å $\leq r \leq$ 1.21 Å. A function of similar form was also obtained by Robinson and Nicholls.[2]

In Fig. 1 we have shown the excitation functions for the bands (2–3), (1–1), (0–1), (1–0), (3–0), and (2–0) of the CO^+ comet tail system, measured in the energy range 0.4–20 keV. As can be seen from the figure, the behavior of the excitation functions is the same for all bands of the CO^+ c.t.s., and for electron energy greater than 0.4 keV is well described by the formula

$$\sigma = \sigma_0 \frac{\ln cE}{E}, \qquad (3)$$

where σ_0 and c are constants; the function $\sigma(E)$ represented by Eq. (3) follows from a calculation of the excitation cross section as a function of energy in the first Born approximation for optically allowed transitions. According to the calculation in this approximation the constant c in Eq. (3) depends only on the excitation energy of the upper level of the system and can be represented in the form $c = 4/(E_{exc} - E_{gnd})$, where E_{exc}

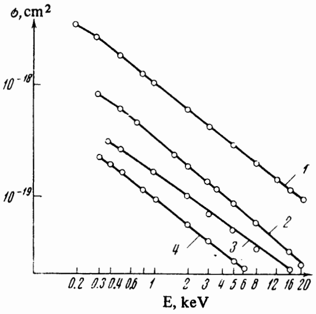

FIG. 2. Excitation functions for the following bands: 1—the (1-1) band of the CO^+ comet tail system; 2—the (1-0) band of the Angström system of CO; 3—the (0-1) band of the CO^+ Baldet-Johnson system; 4—the (1-2) band of the first negative system of N_2^+.

and E_{gnd} are respectively the energies of the excited and ground states of the molecule.

In Fig. 2 we have compared the excitation functions of the bands (1–1) of the CO^+ c.t.s. and (1–2) of the first negative system of N_2^+. As can be seen from Fig. 2, the behavior of the excitation functions of the systems is the same. This could be expected, since the excitation energies of the upper states of these systems are nearly the same, and consequently the constants c in Eq. (3) are almost equal.

2. The Baldet–Johnson System of the CO^+ Ion

The excitation cross sections measured with an electron energy of 4 keV for the (0–1) and (0–0) bands of the Baldet–Johnson system of CO^+ turned out to be respectively 5.4×10^{-20} cm^2 and 7.2×10^{-20} cm^2. In Fig. 2 we have shown the excitation function for the (0–1) band of the CO^+ Baldet–Johnson system. The excitation cross sections for the bands of the CO^+ Baldet–Johnson system are substantially smaller than those for the comet tail system,1) which may be explained by the fact that the excitation energy of the $B^2\Sigma$ state is higher than that for the $A^2\Pi$ state of the CO^+ ion and the transition $B^2\Sigma \rightarrow A^2\Pi$ leads to an additional population of the upper level of the CO^+ comet tail system.

The relative cross sections of the (0–0) and (0–1) bands obtained in the present work (1 and 0.75) are in good agreement with the corresponding values for these bands measured by Skubenich[1] (1 and 0.62). The relative values of σ calculated with the Franck–Condon factor are 1 and 0.63. Thus, good agreement is observed between the theoretical and experimental values.

It can be seen from Fig. 2 that the decrease in excitation cross section of the (0–1) band of the CO^+ Baldet-Johnson system with increasing electron energy occurs more slowly than in the case of the (1–1) band of the CO^+ comet tail system. The observed difference in behavior of the excitation functions of these systems is consistent with Eq. (3), since the constant c for the Baldet–Johnson system is smaller than for the comet tail system of CO^+; this occurs because the $B^2\Sigma$ level (the upper level of the CO^+ Baldet–Johnson system) is located above the $A^2\Pi$ level (the upper level of the CO^+ comet tail system).

3. The Angström System of the CO Molecule

We measured the cross sections of the (0–0) and (1–0) bands of the Angström system of the CO molecule for an energy of 4 keV; these cross sections turned out to be respectively 1.1×10^{-20} cm^2 and 0.6×10^{-20} cm^2. The ratio of the cross sections of these bands is close to the value measured by Skubenich.[1] As can be seen from Fig. 2, the excitation function of the (1–0) band of the CO Angström system for $E > 0.4$ keV also is described by Eq. (3). However, the excitation cross section of this band increases with increasing electron energy more rapidly than the excitation cross section of the bands of the CO^+ ion (the CO^+ comet tail system and the CO^+ Baldet-Johnson system). This is explained by the fact that the excitation energy of the Angström system of the CO molecule is lower than for the comet tail system and the Baldet–Johnson system of the CO^+ ion, and consequently the constant c in Eq. (3) is larger, which leads to this type of change in the behavior of the excitation of the function.

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1)As can be seen from refs. 1 and 7, the most intense bands are the bands (0-0) and (0-1).

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91