ROTATIONAL AND VIBRATIONAL EXCITATIONS OF N_2^+ IONS FORMED IN COLLISIONS BETWEEN INERT GAS ATOMS AND NITROGEN MOLECULES

G. N. POLYAKOVA, V. F. ERKO, Ya. M. FOGEL', A. V. ZATS, and B. M. FIZGEER

Physico-technical Institute, Ukrainian Academy of Sciences

Submitted January 25, 1969

Zh. Eksp. Teor. Fiz. 56, 1851—1855 (June, 1969)

Rotational and vibrational excitations of N_2^+ ions formed in collisions between N_2 molecules and 5—30-keV He, Ne, Ar, Kr, and Xe atoms are investigated. The rotational and vibrational excitations of N_2^+ ions are compared for incident atoms and their corresponding ions. It is concluded that higher rotational and vibrational excitations of N_2^+ ions are induced by atomic impacts than by ionic impacts.

INTRODUCTION

In earlier work[1,2] we analyzed the rotational and vibrational excitations of electronically excited diatomic molecules formed in collisions between N_2 molecules and electrons or various ions. In the presence of an electronic transition there are two possible causes for the rotational and vibrational excitations of diatomic molecules: 1) Reorganization of the electronic shell as a result of the electronic transition, and 2) the action of the incident-particle field on molecules of the target. An analysis of the results obtained by ourselves and by other investigators[2] showed that the rotational excitation of $N_2^+(B^2\Sigma_u^+)$ is induced only by the field of the incident particle, but that the vibrational excitation can be attributed to both of the aforementioned causes.

In our earlier investigations[1,2] the field of the incoming particle was either a pure Coulomb field (that of an electron) or nearly a Coulomb field (that of an ion). It was of interest to compare the rotational and vibrational excitations of $N_2^+(B^2\Sigma_u^+)$ that resulted when nitrogen molecules were bombarded with particles having long-range Coulomb fields, and, as a contrast, particles having short-range fields. In the present work we selected He, Ne, Ar, Kr, and Xe atoms as the particles having short-range fields. Measurements were also obtained with Kr^+ and Xe^+ ions. To compare the rotational and vibrational excitations of $N_2^+(B^2\Sigma_u^+)$ induced by impacts with atoms and their corresponding ions we used data given in[2] for He^+, Ne^+, and Ar^+. The apparatus used to obtain 5—30-keV atoms of inert gases has been described in[3].

As previously, to investigate the rotational and vibrational excitations of $N_2^+(B^2\Sigma_u^+)$ we used bands of the first negative system of N_2^+ (1 n.s. N_2^+) having the wavelengths 4278 Å (0, 1) and 4236 Å (1, 2).

As in our earlier work, the measure of the rotational excitation of $N_2^+(B^2\Sigma_u^+)$ was the deviation of the $N_2^+(B^2\Sigma_u^+)$ ion distribution over rotational levels from the distribution calculated on the basis of Boltzmann's equation. The difference was characterized quantitatively by $\delta = \Delta L_K/L_{K,B}$, where $L_K \equiv \ln(I_K/(K+1))$ and $L_{K,B}$ is the value of L_K for a rotational line with K = 18 when the rotational-line intensity distribution of the band obeys the Boltzmann equation; $\Delta L_K = L_K - L'_{K,B}$ is the difference between L_K and $L_{K,B}$ for the same rotational line; I_K is the intensity of the rotational line corresponding to the rotational quantum number K.

The measure of the vibrational excitation of $N_2^+(B^2\Sigma_u^+)$ that was induced by the field of the bombarding particle was the deviation of the ratio N_1/N_0 (where N_1 and N_0 are the populations of the first and zeroth vibrational levels of N_2^+ in the state $B^2\Sigma_u^+$) from its value calculated according to the Franck-Condon principle for the transition from the $X'\Sigma_g^+$ state of the N_2 molecule to the $B^2\Sigma_u^+$ state of the N_2^+ ion. The ratio N_1/N_0 was calculated using the measured intensity ratio of the 4236 Å and 4278 Å band edges and the transition probabilities given in[4].

The aforementioned rotational line intensities and intensity ratios of 1 n.s. N_2^+ band edges were measured using nitrogen pressures in the collision chamber and equivalent currents of the inert-gas atoms that provided for single collisions between beam atoms and the nitrogen molecules.

EXPERIMENTAL RESULTS AND DISCUSSION

The intensity distribution of rotational lines of the 4278 Å band that had been excited by collisions between fast inert-gas atoms and N_2 molecules differed from the Boltzmann distribution in all the investigated cases. The deviation is illustrated in Fig. 1, which represents the functional relationship $L_K = f((K+1)(K+2))$ for the 4278 Å band excited by 5-keV He atoms. The figure includes, for comparison, the analogous relationship for the 4278 Å band excited by 5-keV He^+ ions. The straight

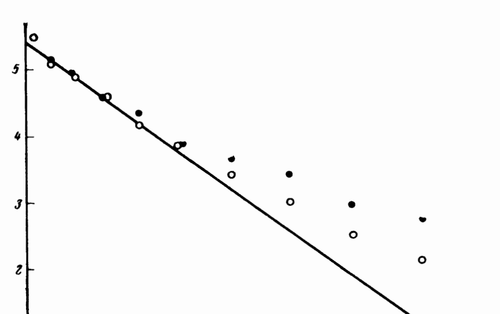

FIG. 1. L_K as a function of (K + 1) (K + 2) for the 4278 Å band, excited by: ● — 5-keV He atoms, and ○ — 5-keV He^+ ions.

Particle	Velocity 10^7cm/sec	δ, %	Particle	Velocity 10^7cm/sec	δ, %
He^+	12,2	10	Ne^0	3,9	42
He^0	12,2	19	Ar^+	3,9	25
He^+	8,65	17	Ar^0	3,9	31
He^0	8,65	29	Kr^+	2,7	31
He^+	5	28	Kr^0	2,7	37
He^0	5	55	Kr^+	1,9	40
Ne^+	5,5	15	Xe^+	2,2	13
Ne^0	5,5	36	Xe^0	2,2	29
Ne^+	3,9	18	Xe^+	1,5	21

line in Fig. 1 represents the Boltzmann distribution of rotational line intensities at 300°K (the temperature of nitrogen in the collision chamber).

Figure 1 shows that the deviation of the rotational line intensity distribution from the Boltzmann distribution is greater for He atoms than for He^+ ions of the same given velocity. The same effect is observed for other velocities of the helium particles and for all the other inert-gas particles. The accompanying table includes the values of δ for the inert-gas atoms and the Kr^+ and Xe^+ ions investigated in the present work, and also for He^+, Ne^+, and Ar^+ ions in[2]. It is seen from the data that δ increases as the velocity of the particle decreases, in the cases of both atoms and ions.

The dependence of N_1/N_0 on the velocity of the incident atom is represented in Fig. 2 for all the investigated atoms. These curves are compared in Fig. 2b, with the corresponding curves for inert-gas ions in[2]. The dashed lines represent N_1/N_0 calculated from the Franck-Condon principle.

The behavior of N_1/N_0 is shown by the curves in Fig. 2a to be identical for the atoms of all the inert gases except Ne. The magnitude of the ratio N_1/N_0 increases as the velocity decreases. For Ne atoms the values of N_1/N_0 are much larger than for the other inert gas atoms. It should be noted, however, that the dependence of N_1/N_0 on the velocity of Ne^+ ions is of the same character as for the other inert-gas ions.

The observed differences in the rotational excitations of $N_2^+(B^2\Sigma_u^+)$ ions between those induced by atomic impacts and by ionic impacts, respectively, can be accounted for by the different characters of the fields belonging to neutral and charged particles. The range of the forces inducing the rotational excitation of $N_2^+(B^2\Sigma_u^+)$ ions must be much smaller in the case of an atom than in the case of an ion.[1)] Therefore in the first case the maximum of $\delta(v)$ must undergo a considerable shift towards lower velocities than in the second case. Since in the investigated velocity range we always have the inequality $\delta_a > \delta_i$ (where δ_a and δ_i are the values of δ for atomic and ionic impacts, respectively), we must also have the inequality $(\delta_a)_{max} > (\delta_i)_{max}$, which means that a higher rotational excitation of N_2^+ will result from an atomic impact than from an ionic impact.

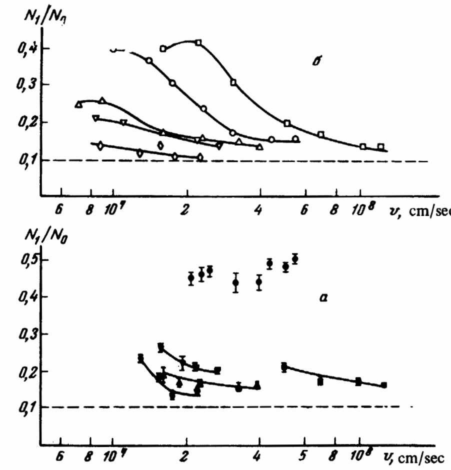

FIG. 2. N_1/N_0 as a function of particle velocity. a – for atomic impacts: ■ – He, ● – Ne, ▲ – Ar, ▼ – Kr, ◆ – Xe; b – for ionic impacts: □ – He^+, ○ – Ne^+, △ – Ar^+, ▽ – Kr^+, ◇ – Xe^+.

Similar considerations indicate that the maximum of the function $N_1/N_0 = f(v)$, which characterizes the degree of vibrational excitation of N_2^+ ions in the case of atomic impacts, will be found at lower velocities than in the case of ionic impacts. Since in the velocity interval used for comparison we have $(N_1/N_0)_a \approx (N_1/N_0)_i$, we can expect that $(N_1/N_0)_{a\,max}$ will exceed $(N_1/N_0)_{i\,max}$; this means that a higher vibrational excitation will result from an atomic impact than from an ionic impact.

The magnitude of the vibrational excitation of $N_2^+(B^2\Sigma_u^+)$ will depend on both the charge of the incident particle and the configuration of its electron shell. This statement is based on the fact that the velocity dependence of N_1/N_0 for Ne atoms differs drastically from the corresponding dependences for the other inert-gas atoms. A similar effect is observed for the Na^+ ion, which possesses the same electron shell configuration as the Ne atom; $(N_1/N_0)_{max}$ for Na^+ ions exceeds the corresponding maxima for the other ions (see Fig. 2 in[2]).

[1)]This is confirmed by a study [5] of the transfer of vibrational energy from excited iodine molecules to unexcited iodine and nitrogen molecules and to helium and neon atoms. From Massey's adiabatic criterion and these observations we calculate 0.75 Å as the range of the forces between neutral particles during the transfer of excitation. It is reasonable to assume the same order of magnitude for the range of forces inducing the rotational excitation of a N_2^+ ion in the case where a fast atom approaches a N_2 molecule. On the other hand, data in [2] indicate 35 Å as the range of the forces inducing the vibrational excitation of N_2^+ $(B^2\Sigma_u^+)$ when He^+, Li^+, Na^+, or K^+ ions approach N_2 molecules.

[1] G. N. Polyakova, Ya. M. Fogel', and A. V. Zats, Zh. Eksp. Teor. Fiz. **52**, 1495 (1967) [Sov. Phys.-JETP **25**, 993 (1967)].

[2] G. N. Polyakova, Ya. M. Fogel', V. F. Erko, A. V. Zats, and A. G. Tolstolutskiĭ, Zh. Eksp. Teor. Fiz. **54**, 374 (1968) [Sov. Phys.-JETP **27**, 201 (1968)].

[3] G. N. Polyakova, V. F. Erko, V. A. Gusev, A. V. Zats, and Ya. M. Fogel', Zh. Eksp. Teor. Fiz. **56**, 161 (1969) [Sov. Phys.-JETP **29**, 91 (1969)].

[4] D. R. Bates, Proc. Roy. Soc. **A196**, 217 (1949).

[5] N. A. Generalov and V. D. Kosynkin, Dokl. Akad. Nauk SSSR **175**, 1033 (1967) [Sov. Phys.-Doklady **12**, 796 (1968)].

Translated by I. Emin
215