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Rotational transitions in collisions between molecular ions: First-order calculations for HD^+-HD^+

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The rotational transitions in HD^+-HD^+ collisions have been studied by using the Coulomb excitation theory of Alder *et al*. The energy range of the calculations extends from 0.1 to 1 eV so that the probability of vibrational excitation at the higher energies is small and at the same time the effect of short-range anisotropies in the ion-ion interaction potential is insignificant. Since V/E is $\ll 1$, the first-order perturbation theory used for our calculations is valid. The rotational transitions induced by the interactions of the charge, dipole, and quadrupole moments of the two molecular ions have been considered. In addition to the single transitions of the ions, simultaneous transitions as well as resonance transfer of energy have been considered. The results have brought out interesting features regarding the relative importance of the various types of transitions involved.

INTRODUCTION

The studies on collision-induced rotational transitions in molecules and their ions have recently been receiving considerable attention because of their importance in the interpretation of the spectroscopic data obtained from interstellar sources and planetary atmosphere. As a result of the experimental difficulties, until now most of the information in this line have been obtained from the theoretical studies. During the last few years a large number of such studies have been performed for atom-molecule and molecule-molecule systems which have led to a better understanding of the various factors influencing rotational transitions. The study of the rotational excitation of molecular ions by collision with neutral atoms has recently been started. However, for rotational transitions in ion-ion collisions, especially when both the collision partners are molecular ions, our present knowledge is very inadequate. Apart from fundamental interest, such processes may be of importance in the planetary sources rich in molecular ions such as O_2^+, N_2^+ (in Earth's ionosphere), and H_2^+ and HD^+ (in the ionosphere of Jupiter).

Watanabe *et al.*[1] studied the vibrational-rotational excitation of HD^+ by collision with the structureless H^+, Li^+, Na^+, and K^+. They used first-order time-dependent perturbation theory with a Rutherford trajectory. This is equivalent to the quantum-mechanical perturbation treatment (which has been applied to electron- and positron-ion collisions by various authors) with Born-Coulomb wave functions.[2] For collisions involving two molecular ions no such study has been made. Such systems are more complicated to deal with but are physically more interesting. In this paper we have studied rotational transitions in the system HD^+-HD^+. HD^+ is the simplest heteronuclear molecular ion with sizable dipole and quadrupole moments so that the influence of different types of intermolecular forces including electrostatic interaction can be studied. For heavy particles the perturbation matrix elements over the Born-Coulomb states can be replaced by the matrix elements of the Coulomb trajectories, avoiding the difficulty of handling Coulomb wave functions. Because of the strongly repulsive forces determining the Coulomb trajectories, the interactions remain very weak so that the first-order perturbation treatment is reliable at least at the lower energies.

We have studied rotational transitions in HD^+-HD^+ collisions in the energy range 0.1–1 eV by using an analogy of the Coulomb excitation theory which has been formulated in an elegant way by Alder *et al.*[3] This theory has previously been used for positron–molecular-ion collisions.[4] Apart from the transitions involving single ions we have also considered simultaneous transitions of the ions and resonance transfer for which the net translational-rotational energy transfer is zero. Resonance transfer, an important channel in systems involving identical species, has been considered recently for a few neutral molecular systems.[5]

THEORY AND CALCULATIONS

We shall apply the first-order time-dependent perturbation theory to the problem of rotational transition in collision between two rigid molecular ions under the assumption of a classical path. The time dependence of the Hamiltonian of such a system arises from the classical relative motion $\vec{R}(t)$ of the two molecules, $\vec{R}$ being the vector distance between the centers of mass of two molecules. This classical trajectory will give a realistic description of the motion since the de Broglie wavelength of such heavy particles is very small. If $\hat{\varphi}_1$ and $\hat{\varphi}_2$ are the angular coordinates of the molecules and $V(\vec{R}(t), \hat{\varphi}_1, \hat{\varphi}_2)$ is the interaction potential between them, the first-order approximation to the matrix element of the scattering matrix between states a and b is given by (in a.u.)

$$S^{(1)}_{ba} = \langle b \,|\, -i \int_{-\infty}^{\infty} e^{iH_0 t} V(\vec{R}(t), \hat{\varphi}_1, \hat{\varphi}_2) e^{-iH_0 t} dt \,|\, a\rangle \ . \qquad (1)$$

Here H_0 is the Hamiltonian without interaction, i.e., that of independent rotation of the two molecules, and a and b are eigenstates of H_0.

This description of the collision is valid when the potential V is much less than the initial relative kinetic energy E_0. In our case, at all energies and orientations $|V|/E_0 \ll 1$ for most of the time during which even a close collision takes place. In this situation the first-order perturbation theory should yield reasonably accurate results.

The classical trajectory is taken to be a Rutherford one since even at the highest energy the strongest spherically symmetric attractive term in the potential (the charge-induced dipole interaction) at the distance of closest approach is less than the Coulomb term by four orders of magnitude.

Thus the ions may be thought of as two cylindrically symmetric, nonoverlapping, rigid, nonpolarizable distribution of charge. The expression for the interaction potential between two such charge distributions in terms of their various multipole moments has been given by Gray[6]

$$V = \sum_{\lambda_1=0}^{2} \sum_{\lambda=0}^{2} \sum_{\eta_1=-\lambda_1}^{\lambda_1} \sum_{\eta_2=-\lambda_2}^{\lambda_2} \frac{4\pi}{2\lambda+1} (-1)^{\lambda_2} \left(\frac{4\pi(2\lambda+1)!}{(2\lambda_1+1)!\,(2\lambda_2+1)!} \right)^{1/2} C(\lambda_1\lambda_2\lambda;\, \eta_1\eta_2\eta_1+\eta_2) \frac{Q_{\lambda_1} Q_{\lambda_2}}{R^{\lambda+1}}$$

$$\times \delta_{\lambda,\lambda_1+\lambda_2} Y_{\lambda_1,\eta_1}(\hat{\varphi}_1) Y_{\lambda_2,\eta_2}(\hat{\varphi}_2) Y^*_{\lambda_1,\eta_1+\eta_2}(\hat{R}) \,. \qquad (2)$$

This approximate expression will be sufficient for our purpose, because (a) the short-range repulsive interaction never becomes significantly large, (b) the multipole expansion in which Q_λ is the 2^λth moment of the charge distribution remains valid, and (c) dipole-induced dipole, dispersion, and other anisotropic interactions can be neglected.

Using the eigenvalue equation for H_0 (the eigenvalues being the sum of rotational eigenergies of the separate ions) and the fact that the eigenfunctions of H_0 are $Y_{j_1 m_1}(\hat{\varphi}_1) Y_{j_2 m_2}(\hat{\varphi}_2)$ for rigid diatomic molecules in Σ states with rotational quantum numbers $(j_1 m_1)$ and $(j_2 m_2)$, respectively, the matrix element (1) can be written as shown by Rabitz and Gordon and by Bhattacharyya *et al.*:

$$S^{(1)}_{j_1^0 m_1^0 j_2^0 m_2^0, j_1 m_1 j_2 m_2} = -i \sum_{\substack{\lambda_1=0 \\ \lambda_1,\lambda_2 \neq 0}}^{2} \sum_{\lambda_2=0}^{2} \frac{(-1)^{\lambda_2}}{(2\lambda+1)} \left(\frac{4\pi(2\lambda+1)!}{(2\lambda_1)!\,(2\lambda_2)!} \right)^{1/2} \left(\frac{(2j_1^0+1)(2j_2^0+1)}{(2j_1+1)(2j_2+1)} \right)^{1/2} C(\lambda_1\lambda_2\lambda;\, \eta_1\eta_2\eta_1+\eta_2) C(j_1^0\lambda_1 j_1;\, 000)$$

$$\times C(j_2^0\lambda_2 j_2;\, 000) C(j_1^0\lambda_1 j_1;\, m_1^0\eta_1 m_1) C(j_2^0\lambda_2 j_2;\, m_2^0\eta_2 m_2) Q_{\lambda_1} Q_{\lambda_2} \delta_{\lambda,\lambda_1+\lambda_2}$$

$$\times \int_{-\infty}^{\infty} \frac{Y^*_{\lambda,\eta_1+\eta_2}(\Theta\Phi)}{R^{\lambda+1}} e^{i\omega t} dt \ , \qquad (3)$$

where Θ and Φ are the angular coordinates of the trajectory and ω is the difference in rotational energy between the initial and final state.

The degeneracy averaged transition probability from the state $(j_1^0 j_2^0)$ to $(j_1 j_2)$ is given by

$$T_{j_1^0 j_2^0 \to j_1 j_2} = \frac{1}{(2j_1^0+1)(2j_2^0+1)} \sum_{m_1 m_2} \sum_{m_1^0 m_2^0} \left| S^{(1)}_{j_1^0 m_1^0 j_2^0 m_2^0, j_1 m_1 j_2 m_2} \right|^2 . \qquad (4)$$

The average relative kinetic energy used in our calculation is

$$E = E_0 - \tfrac{1}{2}\omega \ , \qquad (5)$$

where E_0 is the initial relative kinetic energy and the initial rotational quantum numbers of the two molecules are j_1^0 and j_2^0. Thus the effect of translation ⟷ rotation energy transfer is incorporated in an approximate and indirect way.

In (3) we have replaced the sums over λ_1 and λ_2 by $\lambda_1 = |\Delta j_1|$ and $\lambda_2 = |\Delta j_2|$, when $\Delta j_i = 1$ or 2 only the term with $\lambda_i = 1$ or $\lambda_i = 2$ contributes to the matrix element. But for $\Delta j_i = 0$ (single-molecule transitions) the quadrupolar interaction with $\lambda_i = 2$ also contributes. This term will in general interfere with the monopolar contribution. However, the ranges of the quadrupole-dipole (Q-D) and Q-Q interactions are so small compared to that of the charge-D or charge-Q interaction, that neither the magnitude of the cross section nor the structure of the differential cross section is influenced by these terms.

The time integral in Eq. (3) is very similar to the integral arising in the theory of Coulomb excitation of nuclei. The formulation and the method of evaluation of these integrals have been given by Ter-Martirosyan[7] and Alder *et al.*[3] In the focal system of the hyperbolic orbit, they expressed these integrals over time, $S_{E\lambda,\mu}$, as functions of the scattering angle ϑ and the two variables

$$a = 1/2E \tag{6}$$

and

$$\xi = \frac{a\omega}{v} = \frac{1}{v}\,\frac{\omega}{2E}\,; \tag{7}$$

a is half the distance of closest approach with the average relative kinetic energy and v is the relative velocity corresponding to E.

Using the transformation of Alder *et al.*,

$$S_{E\lambda,\mu} = v^{-1}a^{-\lambda}Y_{\lambda\mu}(\tfrac{1}{2}\pi, 0)I_{\lambda\mu}(\vartheta, \xi)\,, \tag{8}$$

where

$$I_{\lambda\mu}(\vartheta, \xi) = \int_{-\infty}^{\infty} \frac{\exp[i\xi(\epsilon \sinh w + w)][\cosh w + \epsilon + i(\epsilon^2-1)^{1/2}\sinh w]^{\mu}}{(\epsilon\cosh w + 1)^{\lambda+\mu}}\,dw\,, \tag{9}$$

$$\epsilon = \frac{1}{\sin(\vartheta/2)} = \left(1+\frac{b^2}{a^2}\right)^{1/2}, \tag{10}$$

being the eccentricity of the hyperbola where b is the impact parameter.

For $\xi = 0$, i.e., for resonant collision the integrals $I_{\lambda\mu}$ have been analytically evaluated by Alder *et al.* For nonzero ξ the absolute magnitude of $I_{\lambda\mu}$ has been tabulated for selected values of ξ and for $\lambda = 1, 2, 3, 4$ with the allowed μ values by Alder and Winther.[8] From these tables the $I_{\lambda\mu}$ values can be interpolated for other ξ values.

The differential cross section is obtained by multiplying the transition probability for the scattering angle ϑ with the corresponding Rutherford differential cross section $d\sigma_R$

$$d\sigma_R = \tfrac{1}{4}a^2 \sin^{-4}(\vartheta/2)\,d\Omega\,. \tag{11}$$

The dipole moment of HD^+ has been calculated by Saha,[9] and the quadrupole moment by Ray and Barua.[10] In this calculation their values 0.335 and 1.578 a.u., respectively, have been used. This value of the dipole moment of HD^+ is significantly different from the value used by Watanabe *et al.*,[1] who used the value of 0.233 a.u. but did not indicate the source. The value used here is also in agreement with other recent estimates.[11]

RESULTS

In Fig. 1 the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole resonant cross sections are plotted against energy. The condition for dipole-dipole resonance is $|j_1^0 - j_2^0| = 1$, $\Delta j_1 + \Delta j_2 = 0$ and for quadrupole-quadrupole resonance $|j_1^0 - j_2^0| = 2$, $\Delta j_1 + \Delta j_2 = 0$. Resonant energy transfer from one molecule to the other through the D-Q interaction is possible for transitions like $(j_1^0, j_2^0) \rightarrow (j_1, j_2)$ either if $j_1^0 + 1 = 2j_2^0 - 1$ or $j_1^0 = 2j_2^0 + 3$ or the reverse.

From the structure of Eq. (8) we see that since $I(\vartheta, 0)$ is independent of energy so for the (l_1, l_2) resonant transtion

$$S^{(1)\text{res}}_{l_1 l_2} \propto v^{-1}a^{-l} \quad (l = l_1 + l_2) \tag{12}$$

and since $d\sigma_R \propto a^2$ and $a \propto 1/E$

$$\sigma^{\text{res}}_{l_1, l_2} \propto E^{2l-3}\,. \tag{13}$$

Thus $\sigma^{\text{res}}_{D-D}$ increases with energy as E, $\sigma^{\text{res}}_{D-Q}$ as E^3, and $\sigma^{\text{res}}_{Q-Q}$ as E^5.

The expressions for the nonresonant cross sections contain, apart from this factor, another energy-dependent factor $I^2_{\lambda\mu}$ and this rapidly decreases with decreasing energy. Therefore, the rates of decrease of nonresonant cross sections with decreasing energy are much faster than the corresponding resonant cross sections. This is evident from Figs. 2 and 3, which show the depen-

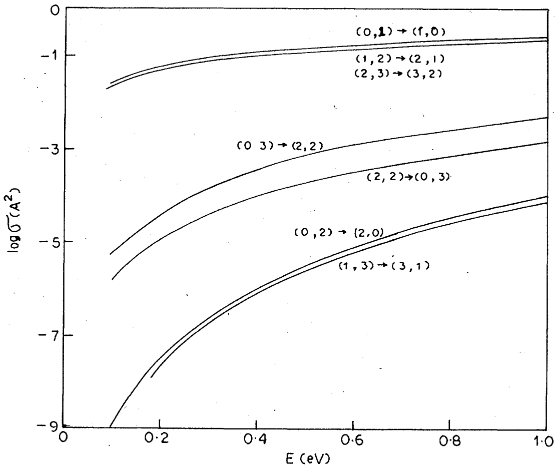

FIG. 1. Total resonant cross sections (D-D, D-Q, and Q-Q) as functions of initial energy.

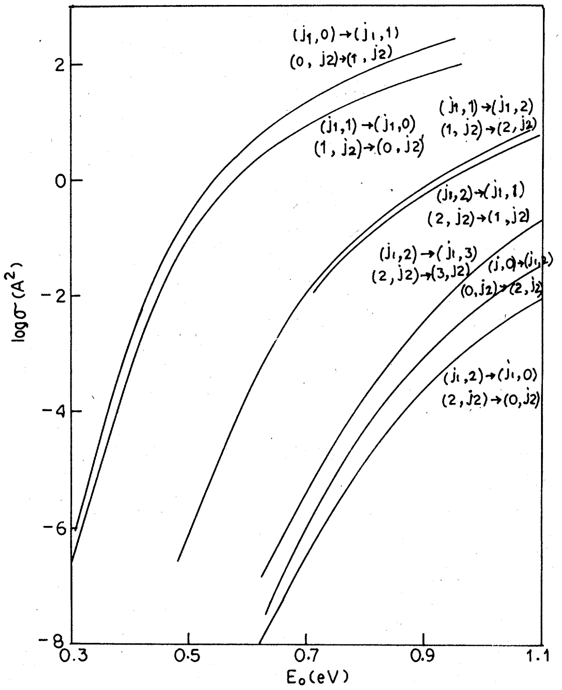

FIG. 2. Total cross sections for single molecular ion transition occurring through the charge-*D* and charge-*Q* interactions as functions of energy.

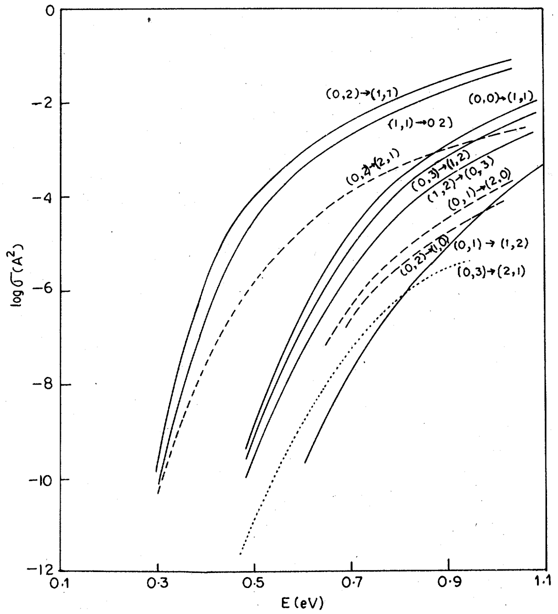

FIG. 3. Total cross sections for simultaneous transition of both the ions as functions of energy. The *D*-*D* transitions are shown by full lines, *D*-*Q* and *Q*-*D* transitions by dashed curves, and the *Q*-*Q* transition by the dotted curve.

dence of single-molecule transition and simultaneous transition cross sections on energy.

We see that when the condition of *D*-*D* resonance is satisfied the total transition cross section below 0.4 eV is wholly dominated by this cross section. If $|j_1^0 - j_2^0| = 2$ the *Q*-*Q* resonance cross section dominates over the single-molecule transition cross sections only below 0.2 or 0.25 eV. However, at such energies almost all the cross sections become negligible. The accidental *D*-*Q* resonance, if any, begins to become important at an energy in between these two values. These energies will be shifted to higher values if we start with the molecules at higher rotational levels where even the single-molecule transitions involve considerable amount of translation $\leftrightarrow$ rotation energy transfer.

At the highest energy considered, the largest resonant *D*-*D*, *D*-*Q*, and *Q*-*Q* cross sections are about 0.28, 3×10^{-3}, and 10^{-4} Å^2, respectively. The charge-dipole cross section with the lowest finite $T \leftrightarrow R$ energy transfer is $(j_1^0, 0) \to (j_1^0, 1)$. This cross section is as high as ~ 200 Å at $E = 0.9$ eV. Thus this low-energy-transfer cross section through a very long-range interaction may be higher by three orders of magnitude than the resonant *D*-*D* cross section. We also note that single-molecule transition cross sections with $\Delta j = 2$ or 1 do not depend on the rotational state of the other molecule. This will not be true if we include all the scattering without change of state that may take place through the quadrupolar interaction.

More significant will be the comparison of the $(0,1) \to (1,0)$ resonant cross section with the $(0,1) \to (2,1)$ or the $(0,1) \to (1,2)$ cross sections as they are caused by interaction terms with the same radial but a different angular dependence, and the same radial and angular dependence, respectively. We see that the $(0,1) \to (2,1)$ cross section is lower than the *D*-*D* resonant cross section by one order of magnitude at 1 eV and by seven orders of magnitude at 0.7 eV. Similar conclusions may be drawn by studying the *D*-*D* nonresonant cross section. It is also interesting to note that at low energies the higher multipole transitions involving low $T \leftrightarrow R$ energy transfer (through one molecule being excited and the other deexcited) contribute a greater amount to the total inelastic cross section than lower multipole transitions involving higher energy transfer.

In Fig. 4 the differential cross sections (multiplied by $2\pi \sin\vartheta$) of some resonant and nonresonant transitions have been plotted. Each of these show a peak whose location depends upon the order of the multipoles through which the transition occurs and then decreases slowly. As expected, the peak shifts to higher angles with increasing multipole order. The *D*-*D* resonance peak is near 70° while

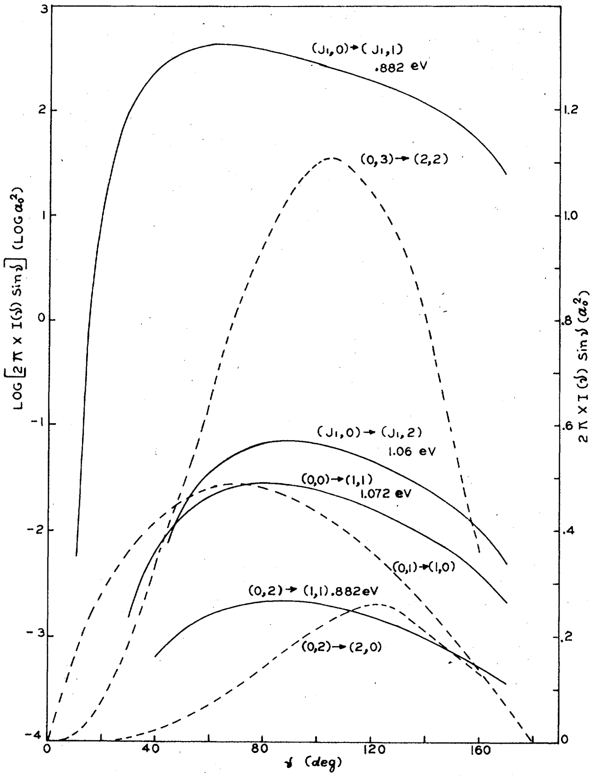

FIG. 4. Some representative resonant and nonresonant differential cross section $I(\vartheta)$ multiplied by $2\pi \sin\vartheta$ patterns shown as functions of the scattering angle ϑ. The nonresonant transitions are shown by full curves; resonant transitions, by dashed curves. The left-hand scale is for nonresonant transition and the right-hand scale for resonant transitions. All resonant curves are for $E_0 = 1$ eV. The $(0,3) \rightarrow (2,2)$ and $(0,2) \rightarrow (2,0)$ differential cross sections have been multiplied by 10^2 and 10^3, respectively, to bring them within the same scale as the $(0,1) \rightarrow (1,0)$ transition.

the D-Q and Q-Q resonance peaks are in the regions $\vartheta = 110°$ and $\vartheta = 125°$, respectively. The peaks also tend to shift to higher angles with decreasing energy. It is to be observed that the curves for transitions involving $T \leftrightarrow R$ energy transfer exhibit peaks at lower angles than the resonant transitions caused through the same term in the interaction potential. But small-angle scattering is in general negligible for transitions involving $T \leftrightarrow R$ energy transfer.

The so-called principle of reciprocity demands the following relation between the cross section $\sigma_{i \to f}$ and $\sigma_{f \to i}$

$$w_i v_i^2 \sigma_{i \to f} = w_f v_f^2 \sigma_{f \to i}, \tag{14}$$

where w_i and w_f are the statistical weight factors for states i and f, v_i and v_f are the relative velocities of the particles for the system in states i and f, respectively.

In the impact theory this relation is not satisfied in general (resonance transitions are important exceptions) because of the difficulty in properly including the effect of translation ↔ rotation energy transfer on the classical trajectory.

If the initial relative kinetic energy is used to describe the trajectory, then the best procedure is to symmetrize the calculated cross sections with respect to the initial and final states. Of course there are various ways of symmetrizing the cross-section expressions. The method adopted by Faisal[4] seems to be the most suitable. He symmetrized his cross section by symmetrizing the distance of closest approach by replacing it by its quantal analog via the correspondence principle so that this quantity remains same for the $i \to f$ and $f \to i$ transitions.

In our approach the effect of energy transfer on the classical trajectory has been incorporated in an approximate way and the principle of reciprocity is automatically satisfied in an approximate way. The method of using the average energy was perhaps the best that could be done until now. This method works more accurately for low-energy transfer and high-energy collisions, and so the principle of reciprocity is satisfied more accurately for such collisions in our approach. Indeed, for $(j_1^0, 0) \to (j_1^0, 1)$ collisions the relation is satisfied to within 5% at 0.9 eV and to within 15% for 0.5 eV. For higher-energy-transfer collisions such as $(j_1^0, 1) \to (j_1^0, 2)$, this relation is obeyed to within 10% at 1.0 eV. The error for $(j_1^0, 2) \to (j_1^0, 3)$ collisions (which involves large energy transfer) becomes large, nearly 25% at 1.0 eV. For simultaneous transitions also the relation is satisfied to within the same accuracy. However, for very large energy transfer (a sizable fraction of the initial relative kinetic energy) the cross section may become uncertain by as much as 50%. But then, the cross section in this energy range become insignificantly small.

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