quenching is written in Eq. (8) in model form. Correct allowance for the quenching would lead to an additional difference between the transport frequencies of the collisions in the excited and the unexcited states, which can only enhance the considered effect.

7) It is precisely this case which is considered in Ref. 1, but in the numerical example formula (4) of Ref. 1 was used at $a \approx 1/6$.

8) In a number of cases it may turn out to be convenient to use Knudsen flow through a capillary, if the indicated difference in the degree of diffuse reflection is not small, and the quenching of the vibrational excitation is produced by collision with the wall.

9) If the source has a broad spectrum that overlaps several vibrational-rotational transitions, it is necessary to take into account in the hydrodynamic equations the evolution of the spectral distribution of the intensity. In this case a self-consistent problem arises, in which the velocity depends on the spectral distribution of the radiation (see the Appendix), and this distribution changes in the course of absorption in the medium in which the drift fluxes are excited.

10) If the velocity u_0 is directed opposite to the wave vector of the radiation (against the beam), then it is necessary to make in (39) the substitutions $\varepsilon \to -\varepsilon$, $\mathrm{Pe} \to -\mathrm{Pe}$. We have then $\varepsilon \sim \mathrm{Pe}/(\mathrm{Pe} + \langle n \rangle \sigma L) \sim 1 (\mathrm{Pe} > \sigma \langle n \rangle L)$; $n_0 \sim u_0/\sigma D \gg n(L) \propto \langle n \rangle$.

---

[1] F. Kh. Gel'mukhanov and A. M. Shalagin, Pis'ma Zh. Eksp. Teor. Fiz. 29, 773 (1979) [JETP Lett. 29, 711 (1979)].

[2] J. E. Bjorkholm, A. A. Ashkin, and D. B. Parson, Appl. Phys. Lett. 27, 534 (1975).

[3] V. D. Antsygin, S. N. Atutov, F. Kh. Gel'mukhanov, G. G. Telegin, and A. M. Shalagin, Pis'ma Zh. Eksp. Teor. Fiz. 30, 262 (1979) [JETP Lett. 30, 243 (1979)].

[4] E. P. Velikhov, V. D. Pis'mennyĭ, and A. T. Rakhimov, Usp. Fiz. Nauk 122, 419 (1977) [Sov. Phys. Usp. 20, 586 (1977)].

[5] N. P. Penkin and T. P. Red'ko, in: Spektrskopiya gazorazryadnoĭ plazmy (Spectroscopy of Gas-Discharge Plasma), Vol. 1, p. 51, Leningr. Univ. Press, 1976.

[6] Yu. M. Gershenzon, S. Ya. Umanskiĭ, and V. B. Rozenshteĭn, in: Khimiya plazmy (Plasma Chemistry), ed. by B. M. Smirnov, Vol. 4, p. 61, Atomizdat, 1977.

[7] A. M. Dykhne and A. N. Starostin, Dokl. Akad. Nauk SSSR 251, 74 (1980) [Sov. Phys. Dokl. 25, 188 (1980)].

[8] C. C. Davis, Digest of Tech. Papers on Conf. on Laser Engineering and Applications, p. 24, Washington, DC, 1979.

[9] K. S. Rutkovskiĭ and K. R. Tokhadze, Zh. Eksp. Teor. Fiz. 75, 408 (1978) [Sov. Phys. JETP 48, 204 (1978)].

[10] A. V. Eletskiĭ, L. A. Palkina, and B. M. Smirnov, Yavleniya perenosa v slaboionizovannoĭ plazme (Transport Phenomena in Weakly Ionized Plasma), Atomizdat, 1975.

[11] V. A. Kas'yanov and A. N. Starostin, Zh. Eksp. Teor. Fiz. 76, 944 (1979) [Sov. Phys. JETP 49, 476 (1979)].

[12] S. G. Rautian and I. I. Sobel'man, Usp. Fiz. Nauk 90, 209 (1966) [Sov. Phys. Usp. 9, 701 (1967)].

[13] L. A. Vaĭnshteĭn, I. I. Sobel'man, and E. A. Yukov, Vozbuzhdenie atomov i ushirenie spektral'nykh liniĭ (Excitation of Atoms and Broadening of Spectral Lines), Nauka, 1979.

[14] F. Kh. Gel'mukhanov and A. M. Shalagin, Zh. Eksp. Teor. Fiz. 77, 461 (1979) [Sov. Phys. JETP 50, 234 (1979)].

[15] L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred (Fluid Mechanics), GITTL, §94, p. 450, (1954) [Pergamon, 1959].

Translated by J. G. Adashko

Rotational relaxation of isotope-substituted molecules and excited complexes produced in muon catalysis

V. N. Ostrovskii and V. I. Ustimov

Leningrad State University

(Submitted 27 March 1980)
Zh. Eksp. Teor. Fiz. 79, 1228–1238 (October 1980)

The cross sections of electron-rotatonal transitions produced in collisions of isotope-substituted molecules with atomic particles are expressed within the framework of the adiabatic approximation in terms of the cross sections of the transitions in the corresponding homonuclear reactions. The general formulas are used to calculate the rates of rotational relaxation of the excited complexes produced in muon catalysis of nuclear reactions. The relaxation rate is determined mainly by transitions with odd change of the rotational quantum number, which are forbidden in homonuclear molecules. It is shown that under experimental conditions the relaxation de-excitation of the complexes is much faster than their breakup into the initial products, thus producing favorable conditions for the nuclear fusion reaction.

PACS numbers: 31.70.Hq, 34.50.Hc

1. INTRODUCTION

Replacement of one of the nuclei in a homonuclear molecule by its isotope leads to a number of new effects. The appearance of a dipole moment and of a vibrational-rotational emission spectrum has been frequently investigated (for homonuclear molecules, the corresponding transitions are forbidden by the selection rules in the dipole approximation). For the HD molecule such a spectrum was observed experimentally,[1] calculated theoretically,[2] and used to register HD molecules in planetary atmospheres and in interstellar medium.[3]

An analogous effect is present in the physics of atomic collisions, namely rotational transitions with odd change of the rotational quantum number, which are strictly forbidden in a homonuclear molecule (if we disregard the low-probability processes accompanied by a change of the nuclear spin of the molecule). Col-

0038-5646/80/100620-06$02.40

lisions with allowance for isotope-substituted molecules have recently attracted attention,[4] but the indicated new effect was not considered.

An interesting (both from the fundamental point of view and for possible applications) system of the type of isotope-substituted molecule arises in the problem of muon catalysis of nuclear fusion reactions. Leaving out some details, which are discussed in the original and in the review articles,[5,6] we recall that the resonant capture

$$t\mu+\mathrm{D}_2\rightarrow[(td\mu)d\cdot 2e], \tag{1.1a}$$

$$t\mu+\mathrm{DT}\rightarrow[(td\mu)t\cdot 2e] \tag{1.1b}$$

results in systems that can be regarded as isotope-substituted molecules of deuterium or tritium, with the role of one of the nuclei played by the mesic molecule $(td\mu)$. The complexes $[(td\mu)d\cdot 2e]$ or $[(td\mu)t\cdot 2e]$ are produced in excited vibrational-rotational states. If the excitation of the complex is lifted by some additional process, then the resonance conditions are violated, the breakup of the complex into the initial products becomes unlikely, and the nuclear fusion reaction in the mesic molecule $(td\mu)$ can proceed effectively enough. Since the initial energy of the collision (1.1) is thermal, the required lifting of the excitation ensures rotational transitions in the complex, e.g., in collisions with the molecules of the medium

$$[(td\mu)d\cdot 2e](J_0)+\mathrm{D}_2\rightarrow[(td\mu)d\cdot 2e](J)+\mathrm{D}_2, \tag{1.2a}$$

$$[(td\mu)t\cdot 2e](J_0)+\mathrm{DT}\rightarrow[(td\mu)t\cdot 2e](J)+\mathrm{DT}, \tag{1.2b}$$

where J_0 and J are the rotational quantum numbers.

In the present paper we obtain the characteristic rates of these processes and show that the principal role is played precisely by those transitions whose possibility is due to the "isotopic" substitution of one of the nuclei (Sec. 3). It turns out that under the conditions of the experiments of Bystritskii *et al.*[7] the rotational relaxation is much faster than the breakup into the initial products, whereas the radiational relaxation plays no role (Sec. 4). It is thus possible to demonstrate satisfaction of a necessary premise for the realization of the fusion reaction.

The proposed theory (Sec. 2) is based on the adiabatic approximation for the description of the rotation of the molecule during the collision, including also the nonadiabatic correction. With account taken of the smallness of the ratio $(M_1-M_2)/2(M_1+M2)(M_1$ and $M_2)$ are the masses of the nuclei], which characterizes the asymmetry of the distribution of the mass in the molecule, it becomes possible to express the cross sections of the various rotational-inelastic collisions in terms of the cross sections for the corresponding homonuclear molecule. This avoids special calculations or experiments for the isotope-substituted molecules, by making simple use of the extensive theoretical and empirical material accumulated by now for processes with homonuclear reactions. Thus, the theory is much simpler here than for the calculation of the dipole moment and of the probability of the radiative transitions, which have a much smaller smallness parameter $m_e(M_1-M_2)/(M_1M_2)$ (m_e and which call for special complicated calculations with allowance for the nonadiabatic connection between the electron and nuclear motions in the molecule.

2. SCATTERING BY ISOTOPE-SUBSTITUTED MOLECULES

In a homonuclear diatomic molecule, the selection rules forbid various collisional rotational transitions, depending on the accompanying change in the electronic state. In investigations of the lifting of such hindrances on account of isotopic substitution, the concrete formulas for the cross sections depend on the electronic transition and on the type of connection between the electronic, spin, and rotational angular momenta of the molecule in the initial and final states (collisions with change of the electronic state are of interest, e.g., because the produced electron-excited molecules are in many cases easier to register). The method used for the theoretical analysis is illustrated below by one of the simplest examples, namely the transition ${}^1\Sigma^{\eta_0}_{g(u)}\rightarrow{}^1\Lambda^{\eta}_{g(u)}$ or ${}^1\Sigma^{\eta_0}_{g(u)}\rightarrow{}^1\Lambda^{\eta}_{u(g)}$, where η_0 and η take on values + or − (Λ is the projection of the mechanical angular momentum of the electrons on the molecule axis). This includes also as a particular case, scattering without an electronic transition for a molecule in the state ${}^1\Sigma^{\pm}_{g(u)}$; the corresponding formulas are used later in Sec. 3 (we recall that most molecules in the ground electronic state have a symmetry ${}^1\Sigma$).

In the considered case, the angular momenta in the initial and final states are usually connected by a type-b Hund rule. For applications, it is convenient to consider transitions between states with definite ± symmetry,[1)] whose wave functions take in the Born-Oppenheimer approximation the form

$$\Psi^J_{M_J\Lambda^\eta,v}=[2(1+\delta_{0\Lambda})]^{-1/2}(\Psi^J_{M_J\Lambda,v}+\eta\Psi^J_{M_J-\Lambda,v}), \tag{2.1}$$

$$\Psi^J_{M_J\Lambda,v}=\left(\frac{2J+1}{4\pi}\right)^{1/2}(-1)^{-M_J-\Lambda}D^J_{-M_J-\Lambda}(\alpha,\beta,0)\varphi_{vJ}\psi_\Lambda,$$

where $\varphi_{vJ}(R)$ and ψ_Λ are respectively the vibrational and electronic wave functions, and v is the vibrational quantum number. The rotational and total angular momenta of the molecule coincide in this case and are equal to J; M_J is its projection on the Z axis of an immobile coordinate system, and $D^J_{-M_J-\Lambda}(\alpha,\beta,0)$ is a Wigner function describing the rotation of the axis connecting the nuclei. The angles α and β coincide with the two first Euler angles that determine the orientation of the system $\xi\eta\zeta$ connected with the molecule (the ζ axis passes through the nuclei), relative to the immobile coordinate system XYZ. The third Euler angle vanishes, since the η axis is chosen to lie in the XY plane.

In the adiabatic approximation (see, e.g., Refs. 8 and 9) one calculates first the scattering amplitude $F_{\nu_0\rightarrow\nu}(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},E,\mathbf{R})$ with a given electronic transition $\nu_0\rightarrow\nu$ for the initial momentum $\mathbf{k}_0$ and the final momentum $\mathbf{k}$ of the relative motion of the colliding particles ($\hat{\mathbf{k}}_0$ and $\hat{\mathbf{k}}$ are unit vectors directed along $\mathbf{k}_0$ and $\mathbf{k}$, and E is the initial energy of the relative motion). The molecule in question can collide with an electron, atom, or another molecule; the state of the latter, to simplify the formulas, is assumed to be unchanged by the collision (for a more general case see Ref. 10). The position of the nuclei of the molecule in the immobile coordinate frame is characterized in this case by the internuclear vector **R**.

The amplitude of scattering with the molecule transition

$$^1\Sigma^{\eta_0},\ v_0J_0 \to {}^1\Lambda^{\eta},\ vJ$$

(v_0 and v are the initial and final vibrational quantum numbers) is determined by a matrix element of $F_{\nu_0\to\nu} \times (\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R})$:

$$F(\nu_0\to\nu;\, v_0J_0M_{J_0} \to vJM_J;\, \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E) = \left[\frac{(2J_0+1)(2J+1)}{32\pi^2(1+\delta_{0\Lambda})}\right]^{1/2} (-1)^{M_J-M_{J_0}+\Lambda}$$

$$\times \langle (D^{J}_{-M_J,-\Lambda} + \eta D^{J}_{-M_J\Lambda})\varphi_{vJ} | F_{\nu_0\to\nu}(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R}) | D^{J_0}_{-M_{J_0}0}\varphi_{v_0J_0}\rangle, \qquad (2.2)$$

where the integration is with respect to **R**. In accordance with the adiabatic approximation, we neglect throughout the change of the rotational energy in the collision compared with the initial and final energies of the collision and with the energy of the electronic transition.

If the vectors $\mathbf{k}_0$ and $\mathbf{k}$ of the initial and final momenta are turned simultaneously around the **R** axis through a certain angle ω, then the scattering amplitude $F_{\nu_0\to\nu}(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R})$ acquires a phase factor $\exp(i\mu\omega)$, where the quantity $\mu = \Lambda - \Lambda_0$ determines the transfer of the angular momentum to the electron shell when the latter is excited. The scattering amplitude must be expanded in the Wigner functions $D^l_{m\mu}(\alpha, \beta, 0)$, where μ takes on the values $\pm(\Lambda - \Lambda_0)$ and $\pm(\Lambda + \Lambda_0)$ (in our case $\Lambda_0 = 0$):

$$F_{\nu_0\to\nu}(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R}) = \sum_{lm\mu} a_{lm\mu}(\nu_0\to\nu | \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R}) D_{m\mu}{}^{l}(\alpha, \beta, 0). \qquad (2.3)$$

Integrating in (2.2) over the angles, we express the differential scattering cross sections in terms of the coefficients $a_{lm\mu}$. Summing the cross sections over M_J and averaging over M_{J_0}, we obtain

$$\sigma_{J_0\to J}({}^1\Sigma^{\eta_0}, v_0 \to {}^1\Lambda^{\eta}, v;\, \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E) = \frac{k}{k_0}(2J+1)\frac{[1+\eta_0\eta\xi(-1)^{J_0+J}]}{(1+\delta_{0\Lambda})}$$

$$\times \sum_{lm} \begin{pmatrix} J & l & J_0 \\ \Lambda & -\Lambda & 0 \end{pmatrix}^2 (2l+1)^{-1} |a^{\Lambda vJ}_{\Sigma v_0J_0}(lm - \Lambda | \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E)|^2, \qquad (2.4)$$

$$a^{\Lambda vJ}_{\Sigma v_0J_0}(lm - \Lambda | \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E) = \int_0^\infty \varphi_{vJ}(R) a_{lm-\Lambda}(\nu_0\to\nu | \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R}) \varphi_{v_0J_0}(R) R^2\, dR, \qquad (2.5)$$

where the usual notation is used for the $3j$-symbols, $\xi = +1$ if the initial and final electronic states have the same parity (u or g) relative to reversal of the sign of the electron coordinates, and $\xi = -1$ in the opposite case.

It is necessary to substitute in the adiabatic-approximation formulas (2.2) and (2.3) the amplitude of the scattering by immobile charges, calculated relative to the mass center cm of the molecule. For a homonuclear molecule this amplitude F^{cm} becomes simultaneously also the amplitude F^c determined relative to the center c of the internuclear segment, and for isotope-substituted molecules the foregoing quantities are connected by a translational phase factor (Ref. 11)[2]

$$F^{cm,is}(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R}) = \exp(i\Delta\mathbf{R}\mathbf{q}) F^{c,is}(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R}), \qquad (2.6)$$

where the vector $\Delta\mathbf{R} = (\mathbf{R}_1 + \mathbf{R}_2)/2$ is directed from the point cm to the point c; $\mathbf{R}_1$ and $\mathbf{R}_2$ are vectors directed from the center of gravity of the isotope-substituted molecule to the corresponding nuclei; $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$ is the momentum transfer. As indicated by Takayanagi,[11] the idea of a calculation based on formula (2.6) was suggested to him by G. F. Drukarev.

The amplitudes $F^{c,is}$ and $F^{c,hom}$, which describe scattering by isotope-substituted and homonuclear molecules, are different because of the difference between the reduced masses μ_{is} and μ_{hom}, of the colliding particles in these two cases. In the Born approximation, the following relation is valid

$$F^{c,is}(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R}) = \frac{\mu_{is}}{\mu_{hom}} F^{c,hom}\left(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, \frac{\mu_{is}}{\mu_{hom}}E, \mathbf{R}\right), \qquad (2.7)$$

and will be assumed approximately satisfied also in the more general case. We finally obtain thus the relation

$$F^{cm,is}(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E, \mathbf{R}) = \frac{\mu_{is}}{\mu_{hom}} \exp(i\Delta\mathbf{R}\mathbf{q}) F^{c,hom}\left(\hat{\mathbf{k}}_0, \hat{\mathbf{k}}, \frac{\mu_{is}}{\mu_{hom}}E, \mathbf{R}\right). \qquad (2.8)$$

We note that for scattering of an electron by a molecule, the ratio μ_{is}/μ_{hom} is quite close to unity.

We substitute (2.8) and (2.3) in (2.2) and expand the translational exponential in bipolar harmonics, after which it becomes possible to integrate over the directions of R and express the differential cross section for scattering by an isotope-substituted molecule in terms of the parameters $a_{lm\mu}$, determined in accordance with Eq. (2.3) for the homonuclear molecule. Averaging over the direction of the vector q, we obtain

$$\sigma_{J_0\to J}({}^1\Sigma^{\eta_0}, v_0 \to {}^1\Lambda^{\eta}, v;\, \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E) = (2J+1)\left(\frac{\mu_{is}}{\mu_{hom}}\right)^2 \frac{k}{k_0}$$

$$\times \sum_{LL'} \sum_{lm} (2L+1)(2L'+1)(2l+1)^{-1} \begin{pmatrix} J & L' & J_0 \\ \Lambda & -\Lambda & 0 \end{pmatrix}^2 \begin{pmatrix} L & l & L' \\ 0 & -\Lambda & \Lambda \end{pmatrix}$$

$$\times \frac{[1+\eta_0\eta\xi(-1)^{J_0+J+L}]}{1+\delta_{0\Lambda}} |f^{\Lambda vJ}_{\Sigma v_0J_0}(L, lm, -\Lambda | \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E)|^2, \qquad (2.9)$$

$$f^{\Lambda vJ}_{\Sigma v_0J_0}(L, lm, -\Lambda | \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, E) = \int_0^\infty \varphi_{vJ}{}^*(R) j_L(\Delta Rq)$$

$$\times a_{lm-\Lambda}\left(\nu_0\to\nu | \hat{\mathbf{k}}_0, \hat{\mathbf{k}}, \frac{\mu_{is}}{\mu_{hom}}E, R\right) \varphi_{v_0J_0}(R) R^2\, dR, \qquad (2.10)$$

where $j_l(z)$ are spherical Bessel functions,

$$\Delta R = \frac{M_1 - M_2}{2(M_1 + M_2)} R.$$

In the theory of molecular spectra, the dependence of vibrational wave functions φ_{vJ} on the rotational number J leads to the so-called vibrational-rotational interaction. If this relatively weak effect is neglected, then the coefficients

$$a^{\Lambda vJ}_{\Sigma v_0J_0},\quad f^{\Lambda vJ}_{\Sigma v_0J_0}$$

do not depend on J_0 and J. We shall henceforth omit for simplicity the symbol for the electron-vibrational transition

$$^1\Sigma^{\eta_0},\ v_0 \to {}^1\Lambda^{\eta},\ v.$$

The next important simplification is obtained if, assuming the Franck-Condon approximation to be satisfied, we replace R by a certain characteristic constant R_0 in the product $j_L a_{lm-\Lambda}$ in (2.10). Comparing the formula for the cross sections obtained in this manner with the formula (2.4) for the homonuclear molecule, we express all the differential cross sections σ^{is} of the rotational transitions for the isotope-substituted molecule, in terms of the cross sections σ^{hom} for scattering by the homonuclear molecule, calculated at one and the same initial relative collision velocity:

$$\sigma^{is}_{J_0\to J}(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},R)=\frac{1}{2}(2J+1)\left(\frac{\mu_{is}}{\mu_{hom}}\right)^2\sum_{Ll}(2l+1)\left[1+\eta_0\eta\xi(-1)^{J_0+J+l}\right]$$
$$\times\begin{pmatrix} J & L & J_0\\ \Lambda & -\Lambda & 0\end{pmatrix}^2 j_l^2(\Delta Rq)\,\sigma^{hom}_{l\to L}\left(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},\frac{\mu_{is}}{\mu_{hom}}E\right). \qquad (2.11)$$

The cross section $\sigma^{\mathrm{hom}}_{l\text{-}L}(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},\mu_{is}E/\mu_{\mathrm{hom}})$ can pertain both to the state Λ^+ and to the state Λ^-, depending on which of the transitions is allowed by the selection rule at given l and L.

The ratio $\Delta R/(R_1+R_2)=(M_1-M_2)/2(M_1+M_2)$ can serve as a small parameter, since its value is 1/6 even for one of the most asymmetrical isotope-substituted molecules HD [actually the expansion (2.11) contains only even powers of $(\Delta R)^2$]. Therefore, being interested in momentum transfers that are not too large, we can expand the spherical Bessel function j_l in a series. For transitions allowed in a homonuclear molecule, l takes on in (2.11) even values, and in the lowest order of the expansion we obtain

$$\sigma^{is}_{J_0\to J}(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},E)=\left(\frac{\mu_{is}}{\mu_{hom}}\right)^2\sigma^{hom}_{J_0\to J}\left(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},\frac{\mu_{is}}{\mu_{hom}}E\right)=\frac{1}{2}(2J+1)\left(\frac{\mu_{is}}{\mu_{hom}}\right)^2$$
$$\times\left[1+\eta\eta_0\xi(-1)^{J_0+J}\right]\sum_{L>\Lambda}\begin{pmatrix} J & L & J_0\\ \Lambda & -\Lambda & 0\end{pmatrix}^2\sigma^{hom}_{0\to L}\left(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},\frac{\mu_{is}}{\mu_{hom}}E\right). \qquad (2.12)$$

For a heteronuclear molecule the factor $\frac{1}{2}[1+\eta\eta_0\xi(-1)^{J_0+J}]$ in the second part of (2.12) must be replaced by unity. The cross section $\sigma^{\mathrm{hom}}_{0\text{-}L}(\mathbf{k}_0,\mathbf{k},\mu_{is}E/\mu_{\mathrm{hom}})$ pertains to a transition into the state ${}^1\Lambda^{\tilde\eta}$, where $\tilde\eta=\eta$ if $L+J_0+J$ is an even number, and $\tilde\eta=-\eta$ in the opposite case. The first equality in (2.12) follows directly from (2.8) with $\Delta R\to 0$. Thus, formula (2.12) expresses simultaneously the cross sections of different collisional rotational transitions in a homonuclear molecule in terms of the cross sections of the transitions from the ground rotational state[10,12] (the last result was obtained recently by a number of workers for the case of scattering without an electronic transition[13,14]).

In the case of transitions that are forbidden in a homonuclear molecule, l takes on only odd values and the cross sections for the isotope-substituted molecules are of the order of smallness $(\Delta R)^2$:

$$\sigma^{is}_{J_0\to J_0+\Delta J}(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},E)=\frac{1}{3}(2J_0+2\Delta J+1)(\Delta Rq)^2$$
$$\times\left(\frac{\mu_{is}}{\mu_{hom}}\right)^2\sum_L\begin{pmatrix} J_0 & L & J_0+\Delta J\\ 0 & -\Lambda & \Lambda\end{pmatrix}^2\sigma^{hom}_{1\to L}\left(\hat{\mathbf{k}}_0,\hat{\mathbf{k}},\frac{\mu_{is}}{\mu_{hom}}E\right). \qquad (2.13)$$

If we confine ourselves to collisions without a change in the electronic state, then for transitions with odd ΔJ, which are forbidden in a homonuclear molecule, we obtain, integrating (2.13) over the angles, the total cross sections for scattering by an isotope-substituted molecule in terms of the momentum-transport cross section $\sigma^{\mathrm{tr,hom}}$ for scattering by a homonuclear molecule:

$$\sigma^{is}_{J_0\to J_0+\Delta J}(E)=\frac{2}{3}(\Delta R)^2k^2(2J_0+2\Delta J+1)\left(\frac{\mu_{is}}{\mu_{hom}}\right)^2$$
$$\times\sum_L\begin{pmatrix} J_0 & L & J_0+\Delta J\\ 0 & 0 & 0\end{pmatrix}^2\sigma^{tr.hom}_{1\to L}\left(\frac{\mu_{is}}{\mu_{hom}}E\right). \qquad (2.14)$$

We indicate in conclusion that the formulas derived here for transitions between single states are valid also for states with arbitrary multiplicity, if the multiplet splitting is small and is not resolved experimentally.[10,12]

3. ROTATIONAL RELAXATION OF EXCITED COMPLEXES IN MUON CATALYSIS

The rate $\lambda^{(r)}_{J_0}$ of departure of molecules from the J_0-the rotational state on account of the collisions (1.2), with allowance for processes with $\Delta J=J-J_0=\pm1;\ \pm2$, is

$$\lambda^{(r)}_{J_0}=n(\alpha_{J_0\to J_0-2}+\alpha_{J_0\to J_0-1}+\alpha_{J_0\to J_0+1}+\alpha_{J_0\to J_0+2}), \qquad (3.1)$$

where n is the concentration of the molecules of the medium, $\alpha_{J_0\to J}=\langle\langle v\sigma_{J_0\to J}\rangle\rangle$ is the rate constant of the collision processes (1.2), and the averaging $\langle\langle\ldots\rangle\rangle$ is carried out over the Maxwellian distribution for the collision velocity v. Collisions with change of rotational states of both molecules make a negligible contribution to the departure rate, as do also processes with $\Delta J>2$ (cf. e.g., the results of numerical calculations for H_2–H_2 collisions[15,16] and HD–H_2 collisions[17]).

The detailed balancing relations make it possible to express all the $\alpha_{J_0\to J}$ in terms of rate constants of collisions of the second kind (i.e., with $J_0>J$). We reduce the latter, in turn, to the rate constants $\alpha_{\Delta J\to 0}$ (k is the Boltzmann constant):

$$\alpha_{J_0+\Delta J\to J_0}=(2J_0+1)(2\Delta J+1)\begin{pmatrix} J_0+\Delta J & J_0 & \Delta J\\ 0 & 0 & 0\end{pmatrix}^2 \qquad (3.2)$$
$$\times\exp[-c(\mu/2kT)^{1/2}\Delta E_{J_0,J_0+\Delta J}]\alpha_{\Delta J\to 0},\quad (\Delta J>0),$$

where T is the temperature of the medium. At $c=0$ this formula is exact within the framework of the adiabatic approximation and neglecting transitions with $\Delta J>2$ [the corresponding formula for the cross sections is obtained from the second equation of (2.12) in the particular case of scattering without an electronic transition]. The exponential dependence on the energy defect of the process

$$\Delta E_{J_0,J_0+\Delta J}=2BJ|\Delta J|$$

($J=J_0$ if $\Delta J>0$, and $J_0+\Delta J$ in the opposite case; B is the rotational constant of the molecule) serves in (3.2) for a semi-empirical allowance for deviations from adiabaticity,[18] since it corresponds to the Massey adiabatic criterion for the cross sections of slow collisions [$\sigma\sim\exp(-\mathrm{const}\,\Delta E/v)$], and can be obtained also in the approximation of two states and in an estimate by perturbation theory. A similar dependence was proposed on the basis of other considerations by others[19] (cf. Ref. 14). The parameter c can be determined, for example, from experimental data, as was done previously,[18] or by approximating the results of other calculations (see below). At high temperature expression (3.2) goes over into the result of the adiabatic theory.

When (3.2) and the explicit expressions for the $3j$ symbols are taken into account, formula (3.1) takes the form

$$\lambda_{J_0}^{(r)}=\frac{3n}{(2J_0+1)}\left\{\left[J_0\exp\left(-2c\left(\frac{\mu}{2kT}\right)^{1/2}B(J_0-1)\right)\right.\right.$$

$$+(J_0+1)\exp\left(-2c\left(\frac{\mu}{2kT}\right)^{1/2}BJ_0-\frac{2B}{kT}(J_0+1)\right)\Big]\alpha_{1\to0}$$

$$+\frac{5}{2}\left[\frac{J_0(J_0-1)}{2J_0-1}\exp\left(-4c\left(\frac{\mu}{2kT}\right)^{1/2}B(J_0-2)\right)\right.$$

$$\left.\left.+\frac{(J_0+1)(J_0+2)}{(2J_0+3)}\exp\left(-4c\left(\frac{\mu}{2kT}\right)^{1/2}BJ_0-2\frac{B}{kT}(2J_0+3)\right)\right]\alpha_{2\to0}\right\}. \quad (3.3)$$

We turn now to the calculation of the independent rate constants $\alpha_{1\to0}$ and $\alpha_{2\to0}$, and consider first the transitions $1\to0$, which are forbidden in the corresponding homonuclear molecule. Equation (2.14) takes in this case the form (we leave out the electron-vibrational transition labels)

$$\sigma_{1\to0}^{is}(E)=\frac{4}{9}(\Delta R)^2E\mu_{is}\left(\frac{\mu_{is}}{\mu_{hom}}\right)^2\sigma_{1\to1}^{tr.\,hom}\left(\frac{\mu_{is}}{\mu_{hom}}E\right). \quad (3.4)$$

Many calculations have been made of the total scattering cross sections $\sigma_{1\to1}$ for H_2–H_2 collisions, using methods of the strong-coupling type (see Refs. 15 and 16 and the bibliography therein), but no momentum-transfer cross sections have been reported although they could be calculated without difficulty. The data available to us on the differential and partial cross sections[15,20,21] are insufficient for a reliable calculation of the momentum-transfer cross section. We indicate finally, that it is possible in principle to use the transport cross sections obtained from diffusion experiments.

Consider two molecules, in which one of the nuclei is replaced by various isotopes. Denoting the pertinent quantities by the indices 1 and 2, we obtain, with the aid of (3.4) the scaling law for the cross sections of the $1\to0$ transitions in these molecules:

$$\frac{\sigma_{1\to0}^{is1}(E)}{\sigma_{1\to0}^{is2}(\mu_{is1}E/\mu_{is2})}=\left(\frac{\mu_{is1}}{\mu_{is2}}\right)^2\left(\frac{\Delta R_1}{\Delta R_2}\right)^2 \quad (3.5)$$

or for the rate constants $\alpha_{1\to0}(T)$

$$\frac{\alpha_{1\to0}^{is1}(T)}{\alpha_{1\to0}^{is2}(\mu_{is1}T/\mu_{is2})}=\frac{\mu_{is1}}{\mu_{is2}}\left(\frac{\Delta R_1}{\Delta R_2}\right)^2, \quad (3.6)$$

where μ_{isi} are the reduced masses of the colliding particles. Thus, the rate constants of interest to us differ only by a factor from those calculated by Chu[17] by the effective-potential method for the process $HD(J=0)+H_2\to HD(J=1)+H_2$. In our case this allows us to use in the simplest manner the available published data.

To calculate the rate constant $\alpha_{2\to0}^{is}$ we retain in (2.11) two terms with $l=0$ and 2, and retain in the spherical Bessel functions $j_l(\Delta Rq)$ only the principal terms of their expansion in the small ΔR:

$$\sigma_{2\to0}^{is}(E)=\left(\frac{\mu_{is}}{\mu_{hom}}\right)^2\left[\sigma_{2\to0}^{hom}\left(\hat{k}_0,\hat{k},\frac{\mu_{is}}{\mu_{hom}}E\right)\right.$$

$$\left.+\frac{16}{225}(\Delta R)^4\mu_{is}^2E^2(1-\hat{k}_0\hat{k})^2\sigma_{2\to2}^{hom}\left(\hat{k}_0,\hat{k},\frac{\mu_{is}}{\mu_{hom}}E\right)\right]. \quad (3.7)$$

The second term turns out to be comparable with the first because it contains an elastic-scattering cross section $\sigma_{2\to2}^{hom}$ that is large compared with $\sigma_{2\to0}^{hom}$. To obviate the need for knowing the differential cross section $\sigma_{2\to2}^{hom}$, we exclude it by using the results of calculations in the similar approximations used by Green[16] for the H_2–H_2 collision and by Chu[17] for the Hd–H_2 collision. We then obtain for the rate constants

$$\alpha_{2\to0}^{is1}(T)=\frac{\mu_{is1}}{\mu_{is2}}\left(\frac{\Delta R_{is1}}{\Delta R_{is2}}\right)^4\alpha_{2\to0}^{is2}\left(\frac{\mu_{is1}}{\mu_{is2}}T\right)$$

$$+\left(\frac{\mu_{is1}}{\mu_{hom}}\right)\left[1-\left(\frac{\Delta R_{is1}}{\Delta R_{is2}}\right)^4\right]\alpha_{2\to0}^{hom}\left(\frac{\mu_{is1}}{\mu_{hom}}T\right), \quad (3.8)$$

where the indices 1 and 2 pertain respectively to the scattering (1.2) and to the Hd–H_2 system.

The rate constant $\alpha_{2\to0}^{is2}$ was taken from the paper by Chu.[17] Inasmuch as Green[16] gives no rate constants, $\alpha_{2\to0}^{hom}$ was calculated from the data of his paper for the cross sections $\sigma_{0\to2}^{hom}$, which were approximated by the analytic formula

$$\sigma_{0\to2}^{hom}(E)=a(E/E_0-1)^{\alpha}, \quad (3.9)$$

where $a=2.264\cdot10^{-17}$ cm^2, $\alpha=1.0421$, and $E_0=0.0441$ eV are in fair agreement with the results of the calculations by Allison and Dalgarno.[21] We prefer Green's data,[16] since the interaction potential used by him is analogous to the potential assumed in Ref. 17.

The figure shows the results of a calculation of $\lambda_{J_0}^{(r)}$ by the described method for the process (1.2) at $J_0=1,2,\ldots,5$ and for liquid-hydrogen density ($n_0=4.25\cdot10^{22}$ cm^{-3}) as a function of temperature. The non-adiabaticity parameter c was determined by least squares, with the results of Chu[17] approximated with the aid of formula (3.2) ($c=6.45\cdot10^{18}$ sec/cm-g).[3)] We note that neglect of transitions with $\Delta J=2$ underestimates the departure rate $\lambda_{J_0}^{(r)}$ by approximately 10–15%, i.e., the principal role is played by transitions with $\Delta J=1$.

4. CONCLUSION

The actual method for practical applications (Sec. 3) of the general results (Sec. 2) was dictated by the tendency to make the simplest possible use of the available published data. If the transport cross sections are simultaneously calculated with the scattering cross sections of the homonuclear molecules, then the determination

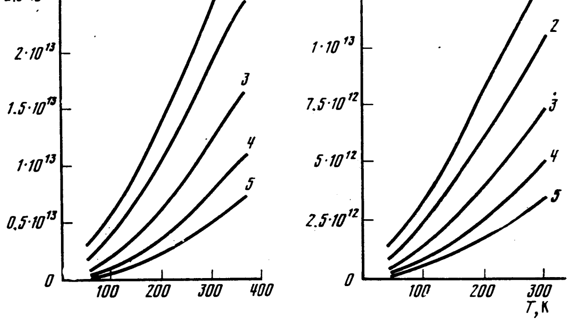

FIG. 1. Rate $\lambda_{J_0}^{(r)}$ of rotational relaxation of excited complexes as a function of temperature at a material density $n_0=4.25\cdot10^{22}$ cm^{-3}: a—the complex $[(td\mu)d\cdot2e](J_0)$, process (1.2a); b—the complex $[(td\mu)t\cdot2e](J_0)$, process (1.2b). The numbers on the curves indicate the values of the initial rotational quantum number J_0.

of the cross sections for the isotope-substituted molecules becomes quite simple. The accuracy of the obtained rate constants $\alpha_{1\to 0}$ and $\alpha_{2\to 0}$ can apparently be regarded as comparable with the accuracy of Chu's calculations.[17] Extrapolation of the data to other transitions entails additional neglect of the transitions with $\Delta J > 2$, which leads to errors of several percent, and also requires a semi-empirical allowance for the nonadiabaticity of the collisions, which can introduce under the most unfavorable conditions (low temperatures, high levels) an error of several dozen percent. This accuracy is fully sufficient for an estimate of the role of the collisional rotational relaxation in muon catalysis.

For a rough estimate of the role of radiative transitions one can assume that the matrix elements of the dipole-moment operator for transitions in the complex $[td\mu)d2e]$ are the same as for the HD molecule, i.e., $\sim 10^{-4}$ D.[4] Since the last quantity is small (cf. Sec. 1), the characteristic rate of radiative relaxation ($\sim 10^{-5}$ sec^{-1}) is smaller by many orders of magnitude than that of the collisional relaxation, so that at matter concentrations corresponding to a liquid or a solid, the former process can be neglected. The density of the medium does not influence the radiative relaxation, whereas the rate of collisional relaxation is proportional according to (3.1) to the density).

The capture rate (1.1) λ^{res} was calculated by Vinitskiĭ *et al.*,[5] where it is given for a material density $n_0 = 4.25 \cdot 10^{22}$ cm^{-3} and for a Maxwellian distribution $\gamma(E, T)$ in the collision energy E for the temperature T:

$$\gamma(E,T)=\left(\frac{27E}{2\pi kT}\right)^{1/2}\frac{1}{kT}\exp\left(\frac{-3E}{2kT}\right). \tag{4.1}$$

The rate λ_d of the inverse process—the breakup of the excited complex into the initial products—can be obtained with the aid of the detailed-balancing relation, which in this case takes the form

$$\lambda_d=\lambda^{res}\frac{\mu^2 v_0}{n_0\gamma(E_0,T)}\frac{4\pi}{(2\pi\hbar)^3}=\frac{\lambda^{res}}{n_0}\left(\frac{\mu kT}{3\hbar^2\pi}\right)^{3/2}\exp\left(\frac{3E_0}{2kT}\right), \tag{4.2}$$

where v_0 is the relative rate of the colliding particles (1.1) (or of the breakup products) and μ is their reduced mass ($E_0 = \mu v_0^2/2$).

The values of λ^{res} are given in Refs. 5 and 6 for a temperature T equal to the resonant collision energy E_r. For the process (1.1) we have $E_r = 0.053$ eV,[56] and it follows from (4.2) that $\lambda_d = 3.7 \cdot 10^2\ \lambda^{res}$ ($\lambda^{res} = 9.4 \cdot 10^7$ sec^{-1}, Refs. 5 and 6). For the analogous process with production of the $(dd\mu)$ mesic molecule

$$d\mu + D_2 \to [(dd\mu)d\cdot 2e]^*. \tag{4.3}$$

$E_r = 0.07$ eV,[5,6] and from (4.2) we get $\lambda_d = 4.0 \cdot 10^2\ \lambda^{res}$ ($\lambda^{res} = 6.3 \cdot 10^5$ sec^{-1}, Refs. 5 and 6).

At a temperature ~300 K, the rate of collisional rotational relaxation, calculated in the present paper is $\lambda^{rel} \sim 10^{12}$ sec^{-1} and increases with rising temperature. It can thus be assumed that prior to their breakup into the initial products, all the complexes lose their excitation via collisions with the molecules of the medium, after which their decay becomes unlikely. This ensures the existence of the $(td\mu)$ and $(dd\mu)$ molecules over a time sufficient for the nuclear reaction to take place.

The authors are deeply grateful to L. I. Ponomarev, who called their attention to the problem of rotational relaxation in muon catalysis and for making many helpful remarks during the discussion of the work.

---

1) For the states Σ, the electronic wave functions ψ_Λ already have a definite symmetry, + or −. Therefore, it suffices in this case to put formally in (2.1) and (2.2) $\eta = 1$ for both the + and the − states.

2) Unless otherwise indicated, we use atomic units throughout.

3) Another and apparently less accurate value $c = 3.3 \pm 0.4) \cdot 10^{19}$ sec/cm-g was deduced in Ref. 18 from the experimental data under certain assumptions concerning the mechanisms of population of the rotational levels in a low-temperature plasma.

---

[1] G. Hertzberg, Nature **166**, 363 (1950). R. A. Durie and G. Herzberg, Cand. J. Phys. **38**, 806 (1960).

[2] D. M. Bishop and L. M. Cheung, Chem. Phys. Lett. **55**, 593 (1978); A. L. Ford and J. C. Browne, Phys. Rev. **A16**, 1992 (1977).

[3] J. T. Trauger, F. L. Roesler, N. L. Carleton, and W. A. Traub, Astrophys. J. **184**, L137 (1973).

[4] E. S. Chang and S.-T. Wong, Phys. Rev. Lett. **38**, 1327 (1977).

[5] S. I. Vinitskii, L. I. Ponomarev, T. P. Puzynina, I. V. Puzynin, L. N. Somov, and M. P. Faifman, Zh. Eksp. Teor. Fiz. **74**, 849 (1978) [Sov. Phys. JETP **47**, 444 (1978)].

[6] L. I. Ponomarev, Priroda, No. 8, 8 (1979).

[7] V. M. Bystritskiĭ, V. P. Dzhelepov, V. I. Petrukhin, A. I. Rudenko, L. N. Somov, V. M. Suvorov, V. V. Fil'chenkov, G. Hemnitz, N. N. Khovanskiĭ, B. A. Konomenko, and D. Horvath, Zh. Eksp. Teor. Fiz. **76**, 460 (1979) [Sov. Phys. JETP **49**, 232 (1979)].

[8] Yu. D. Oksyuk, Zh. Eksp. Teor. Fiz. **49**, 1261 (1965) [Sov. Phys. JETP 22, 873 (1966)].

[9] K. Takayanagi and Y. Itikawa, Adv. Phys. **6**, 105 (1970).

[10] V. N. Ostrovskii and V. I. Ustimov, Connections between the Cross sections of Rotational Transitions in Collisions of Diatomic Molecules (Manuscript depositet at VINITI 2 January 1980, No. 35-80 Dep.)

[11] K. Takayanagi, J. Phys. Soc. Japan **28**, 1527 (1970). S. Hara, *ibid* **30**, 819 (1971).

[12] B. P. Lavrov, V. N. Ostrovskiĭ, and V. I. Ustimov, Pis'ma Zh. Tekh. Fiz. **5**, 355 (1979) [Sov. Phys. Tech. Phys. Lett. **5**, 142 (1979)].

[13] S.-I Chu, A. Dalgarno, Proc. Roy. Soc. **A342**, 191 (1975). R. Goldflam, D. J. Kouri, S. Green, J. Chem. Phys. **67**, 4631 (1978).

[14] D. A. Varshalovich and V. K. Khersonsky, Astrophys. Lett. **18**, 167 (1977).

[15] G. Zarur and H. Rabitz, J. Chem. Phys. **60**, 2057 (1974). T. G. Heil and D. J. Kouri, Chem. Phys. Lett. **40**, 375 (1976). T. G. Heil, S. G. Green, and D. J. Kouri, J. Chem. Phys. **68**, 2562 (1978).

[16] S. Green, J. Chem. Phys. **62**, 2271 (1975).

[17] S.-K. Chu, J. Chem. Phys. **62**, 4089 (1975).

[19] B. P. Lavrov, V. N. Ostrovskiĭ, and V. I. Ustimov, Role of Electrons in Formation of Nonequilibrium Distributions of Molecules over the Rotational Levels in Low-Pressure Plasma (Manuscript No. 4199079 Dep, deposited at VINITI 10 December 1979).

[20] W. D. Davidson, Proc. Roy. Soc. **A280**, 227 (1964).

[21] A. C. Allison and A. Dalgarno, Proc. Phys. Soc. **90**, 609 (1970).

Translated by J. G. Adashko