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Gyroscopic Effect in Low-Energy Classical Capture of a Rotating Quadrupolar Diatom by an Ion[†]

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The low-energy capture of homonuclear diatoms by ions is due mainly to the long-range part of the interpartner potential with leading terms that correspond to charge−quadrupole interaction and charge-induced dipole interaction. The capture dynamics is described by the perturbed-rotor adiabatic potentials and the Coriolis interaction between manifold of states that belong to a given value of the intrinsic angular momentum. When the latter is large enough, it can noticeably affect the capture cross section calculated in the adiabatic channel approximation due to the gyroscopic property of a rotating diatom. This paper presents the low-energy (low-temperature) state-selected partial and mean capture cross sections (rate coefficients) for the charge−quadrupole interaction that include the gyroscopic effect (decoupling of intrinsic angular momentum from the collision axis), quantum correction for the diatom rotation, and the correction for the charge-induced dipole interaction. These results complement recent studies on the gyroscopic effect in the quantum regime of diatom−ion capture (Dashevskaya, E. I.; Litvin, I.; Nikitin, E. E.; Troe, J. *J. Chem. Phys.* **2004**, *120*, 9989−9997).

1. Introduction

Accurate statistical theories of chemical reactions combine quantum dynamics of complex formation and decay with a statistical description of intracomplex redistribution of the available energy.[1−4] For noticeably exothermic reactions, the reaction cross section (the rate coefficient) can be often identified with similar characteristics for the complex formation.[5,6] If, in addition, the entrance part of the potential energy surface (PES) possesses no barrier, and the collision energy (translational temperature) is low enough, then the formation of the complex is governed mainly by a long-range part of the interaction. Since quite often this part of the interaction is known reasonably well, the ambiguities that are normally associated with selection of PES disappear and the whole problem becomes purely dynamical: calculation of the complex formation (capture) cross section for a known interaction. The dynamics of the complex formation might still be quite complicated since the approach of reagents is accompanied by the energy transfer between different modes of collision partners. In this respect, the capture of a neutral diatomic molecule by an ion at not too high energies represents a simple case, since the vibration of the former can be adiabatically decoupled from its rotation and the relative motion, and the internal structure of the ion does not affect the capture. The interaction between rotation of a diatom and relative motion can be easily handled numerically, both classically and quantum mechanically, as was accomplished in a number of works. Our earlier work on this topic was mainly concerned with calculation of the rate coefficients for ion−diatom capture in the Boltzmannian ensemble for different representative cases of the interaction potentials.[7,8] In this work, the relative motion was treated classically. The rotation was described either classically (for temperatures T noticeably above the characteristic rotational temperature $T_{\mathrm{rot}} = B/k_{\mathrm{B}}$ with B being the rotational constants of the diatom) or quantum mechanically (for $T \leq T_{\mathrm{rot}}$) within the adiabatic channel approximation.[9,10] The latter assumes that the projection of the intrinsic angular momentum onto the collision axis is conserved, which is justified for a weak Coriolis interaction, at least in the region of centrifugal barriers. For canonical ensembles, this is indeed so provided that the moment of inertia of a diatom is appreciably lower than the moment of inertia of the collision complex in the capture configuration which guarantees that the mean intrinsic angular momentum is small compared to the typical relative angular momentum for the capture.

This situation may change when one passes from partners out of a single canonical ensemble to two different canonical ensembles (as is the case in recent work[11,12]) or rotationally selected partners. Here, it can occur that the intrinsic angular momentum is comparable to the typical capture relative angular momentum especially in the region of low collisions energies, $E \ll B$ (or translational temperatures, $T \ll T_{\mathrm{rot}}$). Under the latter condition, the ion−molecule interaction can be simplified and written as the expectation value of the original potential averaged over unperturbed rotational motion of the diatom (the so-called rotationally adiabatic perturbed-rotor, RAPR, approximation). The ion−diatom Hamiltonian with this interaction corresponds to the conserved value of the intrinsic angular momentum but takes into account the Coriolis interaction omitted in the adiabatic channel (AC) approximation. The capture cross sections calculated in RAPR approximation may differ from the AC cross section because of the gyroscopic effect of the rotor ignored in the AC approximation.

The above sets the scene for discussion of the capture dynamics of rotationally excited homonuclear molecules by ions at low collision energies, when the capture occurs under the action of charge−quadrupole potential. In principle, the capture

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cross sections can be calculated by solving j-diagonal quantum capture equations as discussed recently.[13] However, in view of the extremely rapid convergence of the quantum cross sections to the AC cross sections for lower rotational states of a diatom,[13] we can use classical mechanics for the description of relative motion unless we want to enter the ultralow energies (s-wave scattering). In addition, we can use classical mechanics for the description of rotation since we are interested in the capture of scattering of rotationally excited molecules. We therefore adhere to the fully classical counterpart of our previous quantum study of capture.

Actually, the present study is the classical analogy of the locking of the intrinsic quantum angular momentum to the collision axis, a phenomenon studied in detail for atomic collisions (see, e.g., ref 14). A byproduct of this study is a direct test of the main assumption of the AC approach.

The paper is organized as follows. In section 2, we discuss the representation of classical ion−diatom Hamiltonians in the rotationally adiabatic approximation. Section 3 is devoted to further approximations for the rotationally adiabatic Hamiltonians, namely, the AC and flywheel (FW) Hamiltonians. In section 4, we present the results of numerical calculations of the gyroscopic effect for the charge−quadrupole capture. In section 5, we discuss the results which incorporate corrections for quantized rotation of a diatom and for the charge-induced dipole interaction. In conclusion, we summarize our findings.

2. Rotationally Adiabatic Hamiltonian and Capture Cross Section for Diatom−Ion (atom) System

A classical Hamiltonian for a rigid rotor−atom (ion) system (both in closed electronic states) after the separation of the center-of-mass motion, reads

$$H(\mathbf{P},\mathbf{R},\mathbf{j},\gamma) = \frac{\mathbf{P}_R^{\ 2}}{2m} + \frac{\mathbf{j}^2}{2I} + U(R,\gamma) \tag{1}$$

where $\mathbf{R}$ is the vector between the atom and the diatom center-of-mass, m is the reduced mass of the partners, $\mathbf{P}_R$ is the vectorial momentum of the relative motion which is conjugate to $\mathbf{R}$, $\mathbf{j}$ is the angular momentum of a rotor, I is its moment of inertia, and γ is the angle between $\mathbf{R}$ and the rotor axis. In eq 1, the angle γ is a complicated function of polar and azimuthal angles of the molecular axis $\mathbf{n}$ and the collision axis $\mathbf{R}$. The Hamiltonian in eq 1 contains five degrees of freedom, that is, it contains 10 dynamical variables (five coordinates and five conjugate momenta). This Hamiltonian has been used for the calculation of the capture rate coefficients for different types of interaction potentials for the canonical (translational and rotational) ensemble of collision partners.[7] Because the initial conditions of a single trajectory include quite a number of parameters, the random selection of theses parameters from the Boltzmannian translational−rotational distribution function is an appropriate choice of the averaging. It is difficult to get however, from the results obtained, information about rate coefficients for a diatomic partner in a given rotational state, since many features of an individual state become washed out in the averaging procedure.

To simplify the capture problem and decrease the set of parameters that enter into the capture cross section and capture rate coefficient for a state-selected diatom, one tries to reduce the number of dynamical variables. This is possible by taking into account the conservation of the total angular momentum of a colliding pair and by introducing appropriate dynamical approximation into the Hamiltonian. If one explicitly accounts for the conservation of the total angular momentum, then the number of dynamical variables can be reduced to six.[15] Examples of such Hamiltonians in different angular variables can be found, for instance, in the book ref 16 and the articles refs 17 and 18.

Still other dynamical approximations correspond to the adiabatic limits of the Hamiltonian in eq 1 with respect to the rotation of the diatom. The validity of these approximations is determined by the value of a single parameter, the Massey parameter ς, which is the ratio of the rotational frequency of the diatom to the angular velocity of the collision axis. In the adiabatic approximation, one introduces the adiabatic potentials $V_{\nu,\omega}(R)$ which originate from the two last terms in the rhs of eq 1 after introducing new action variables ν and ω. The variable ω is the projection of the rotor angular momentum onto the collision axis, and ν is a variable which is adiabatically correlated with j at the limit $R \rightarrow \infty$. The adiabatic criterion $\varsigma \gg 1$ guarantees that ν is nearly conserved in the course of the collision; as for ω, it is not conserved since asymptotically different ω states correlate (for a given ν) with a degenerate rotor state.

Different types of AC potentials $V_{\nu,\omega}^{\mathrm{AC}}(R)$ for quantized rotational states were presented in refs 19 and 20. One of the approximations in these calculations is the so-called weak-field expansion, which represents $V_{\nu,\omega}^{\mathrm{AC}}(R)$ as a power series in the ratio of the interaction parameter to the spacing between the rotational states of the diatom. The leading terms in this expansion correspond to the perturbed-rotor (PR) limit when ν is identified with j, and $V_{\nu,\omega}^{\mathrm{PR}}(R)$ is written as a sum of the unperturbed-rotor energy plus the expectation value of $U(R,\gamma)$ for given j and ω values. The classical expression for the latter quantity in the PR limit is obtained from $U(R,\gamma)$ by averaging it over the angle of the proper rotation of the diatom, the angle variable α_j which is conjugate to j. In what follows, we assume the validity of the PR limit which is applicable for low collision energies.[21] The averaging of $U(R,\gamma)$ over α_j with constant j,ω is accomplished with the help of the relation $\cos\gamma = (1 - \omega^2/j^2)^{1/2}\cos\alpha_j$, appropriate for the PR approximation. This means that ACPR potentials $V_{j,\omega}^{\mathrm{ACPR}}(R)$ can actually be written as $V_{j,\omega}^{\mathrm{ACPR}}(R) = j^2/2I + V^{\mathrm{ACPR}}(R,\omega/j)$, and the constant part of it can be omitted. The rotationally adiabatic (RA) Hamiltonian in the PR limit, H^{RAPR} is obtained from expression 1 by replacing $U(R,\gamma)$ with ACPR potentials $V^{\mathrm{ACPR}}(R,\omega/j)$, passing from the SF frame to the BF frame, and considering ω as a dynamical variable, $\omega \equiv p_\phi$, both in the ACPR potential and in the centrifugal energy. The latter step is done by expressing the square of the relative angular momentum ℓ^2 through the total angular momentum J (conserved), intrinsic angular momentum j (conserved in the adiabatic approximation), action variable p_ϕ, and the conjugate angle ϕ. All this yields the RAPR Hamiltonian

$$H^{\mathrm{RAPR}} = \frac{p_R^{\ 2}}{2\mu} + \frac{\ell^2}{2\mu R^2} + V^{\mathrm{ACPR}}(R,\xi) \tag{2}$$

where the square of the relative angular momentum ℓ^2 and the fractional projection of the intrinsic angular momentum onto the collision axis $\xi = p_\phi/j$ are expressed through action-angle variables

$$\ell^2(p_\phi,\phi;J,j) = J^2 + j^2 - 2p_\phi^{\ 2} - 2\sqrt{J^2 - p_\phi^{\ 2}}\,\sqrt{j^2 - p_\phi^{\ 2}}\cos\phi$$
$$\xi = p_\phi/j \tag{3}$$

The Hamiltonian in eq 2 with account taken for eq 3 is written in terms of the conjugate variables, $H^{\mathrm{RAPR}} = H^{\mathrm{RAPR}}(p_R,R,p_\phi,\phi;J,j)$, and therefore it immediately generates equations of motion for the radial separation between the fragments $R(t)$ and for the precessional motion of the intrinsic angular momentum in the BF frame in terms of $p_\phi(t)$ and $\phi(t)$. Note that the last term in the expression for ℓ^2 is responsible for the Coriolis interaction in the BF frame which manifests itself as a gyroscopic effect in the SF frame. Here and below, the semicolon in the arguments of the Hamiltonians (e.g., in H^{RAPR}) separates the dynamical variables from the parameters.

The mean capture cross section (for rotationally unpolarized diatom) $\bar{S}^{\mathrm{RAPR}}(E, j)$ is expressed as an average of the partial capture cross section (for rotationally polarized diatoms), $S^{\mathrm{RAPR}}(E,j,\xi_i)$, with the polarization state defined through the initial value of the reduced projection $\xi_i = p_{\phi,i}/j$ of $\mathbf{j}$ onto the vector of the initial relative velocity $\mathbf{v}$ of the colliding partners. In turn, $S^{\mathrm{RAPR}}(E,j,\xi_i)$ is determined by the mean capture probability $P^{\mathrm{RAPR}}(E,j,\xi_i,J)$

$$\bar{S}^{\mathrm{RAPR}}(E,j) = \int_0^1 S^{\mathrm{RAPR}}(E,j,\xi_i)\,\mathrm{d}\xi_i$$

$$S^{\mathrm{RAPR}}(E,j,\xi_i) = \frac{\pi}{2\mu E}\int_j^\infty P^{\mathrm{RAPR}}(E,j,\xi_i,J)2J\,\mathrm{d}J$$

$$P^{\mathrm{RAPR}}(E,j,\xi_i,J) = \langle P_{\mathrm{traj}}^{\mathrm{RAPR}}(E,j,\xi_i,J,\phi_i)\rangle_{\phi_i} \tag{4}$$

Here, E is the collision energy, $P_{\mathrm{traj}}^{\mathrm{RAPR}}$ is the classical capture probability for a single trajectory (zero or one) that depends on the initial conditions ξ_i and ϕ_i, and $\langle ...\rangle_{\phi_i}$ means the averaging over initial angles ϕ_i. Following our earlier work, we identify the capture (when the probability equals unity) with a moment when the potential energy between the fragments substantially exceeds the initial energy.

For brevity of notation, we adopt the following: the PR abbreviation will be dropped since the PR approximation is used everywhere; the AC abbreviation will mean the fully classical AC approximation, while QAC will stand for the AC approximation when the rotation of the diatom is quantal. A list of abbreviations is given in Appendix A.

3. Adiabatic Channel and Flywheel Approximations

Under additional assumptions, the adiabatic Hamiltonian in eq 2 can be simplified further: either one assumes the conservation of the projection of the intrinsic angular momentum onto the collision axis during the passage over the potential barriers or the conservation of the direction of the intrinsic angular momentum in the space. The former assumption is the basis of the well-known AC approximation, while the latter, introduced in this paper, can be called, by obvious reason, the FW approximation. In the nomenclature used in the theory of atom−atom (ion) collisions[22] with the intrinsic angular momentum identified with the electronic angular momentum of a partner, the AC and FW approximations correspond to the Hund coupling cases *b* and *d* or to their extensions for atom−molecule collisions.[23]

Clearly, AC and FW approximations correspond to two opposite limits of the adiabatic Hamiltonian. The criterion that defines these two limits can be derived from the following qualitative considerations. Conservation of p_ϕ, that is neglecting the Coriolis interaction, means that the angle-dependent part in the expression for ℓ^2 in eq 3 can be averaged over the precession angle ϕ. This is a legitimate procedure provided the precession frequency $\dot{\phi}$ of a diatom is high compared to the inverse of a certain characteristic time τ of the relative motion. For the capture process, $\dot{\phi}$ can be identified as the precession frequency at the barrier maximum and τ with the inverse of the frequency of rotation of the molecular axis. For an estimate, we write

$$\dot{\phi} = 2V^{\mathrm{AC}}(R,p_\phi/j)/\partial p_\phi \approx V^{\mathrm{AC}}(R,p_\phi/j)/j$$

$$1/\tau = \partial(\ell^2/2\mu R_{\mathrm{c}}{}^2)/\partial\ell \approx (\ell^2/2\mu R_{\mathrm{c}}{}^2)/\ell \tag{5}$$

where R_{c} is the capture distance. Since the capture condition is formulated as compensation of the attractive potential and the repulsive centrifugal energy, that is, $V^{\mathrm{ACPR}}(R,p_\phi/j) \approx \ell^2/2\mu R_{\mathrm{c}}^2$, we can write the condition of the applicability of the AC approximation, $\dot{\phi}\tau \gg 1$, in the form

$$j/\bar{\ell} \ll 1 \tag{6}$$

where $\bar{\ell}$ is a typical angular momentum for the capture. We thus consider inequality eq 6 as the condition of applicability of the AC approximation.

Conservation of $\mathbf{j}$ can be regarded as a reasonable approximation if $\mathbf{j}$ remains close, in the course of the collision, to the exactly conserved vector of the total angular momentum $\mathbf{J}$. Due to the relation $\mathbf{J} = \mathbf{j} + \mathbf{l}$, near conservation of $\mathbf{j}$ is possible provided that

$$j/\bar{\ell} \gg 1 \tag{7}$$

We therefore consider inequality eq 7 as the condition of applicability of the FW approximation.

From eqs 6 and 7, it is expected that the gyroscopic effect will noticeably show up for such values of intrinsic momentum j which are of the order of $\bar{\ell}$; therefore, in these cases, the rotation of the diatom can be considered classical, provided the capture is adequately described by classical mechanics. To roughly estimate $\bar{\ell}$ as a function of classical dynamical parameters, we assume that capture occurs under the action of the charge−quadrupole potential $V^{\mathrm{AC}} \propto qQ/R^3$ and resort to the dimensional arguments. From the latter, it follows that $\bar{\ell} \approx E^{1/6}\mu^{1/2}|qQ|^{1/3}$. We note in passing that, for canonical ensembles, according to condition eq 6, the gyroscopic effect is not noticeable if the moment of inertia of a diatom I is appreciably lower than the moment of inertia of the collision complex in the capture configuration, μR_{c}^2. We will discuss now the AC and FW Hamiltonians as well as AC and FW capture cross sections.

AC Hamiltonian and Cross Sections. The AC Hamiltonian is obtained from the RA Hamiltonian by dropping the Coriolis interaction term (the last term in the rhs expression for ℓ^2 in eq 3). Then, ϕ becomes an ignorable angle, and p_ϕ becomes a constant, $p_\phi = \omega$. Hence

$$H^{\mathrm{AC}}(p_R,R;j,\omega,J) = \frac{p_R{}^2}{2\mu} + \frac{J^2 + j^2 - 2\omega^2}{2\mu R^2} + V^{\mathrm{AC}}(R,\omega/j) \tag{8}$$

Condition eq 6 means that the AC Hamiltonian in eq 8 can (and actually should) be simplified, for consistency reasons, by neglecting the two last terms in the expression for the centrifugal energy and, therefore, by identifying J with ℓ. Within this change, two parameters ω and j can be absorbed into a single parameter $\xi_{\mathrm{AC}} = \omega/j$, yielding

$$H^{\mathrm{AC}}(p_R,R;J,\xi_{\mathrm{AC}}) = \frac{p_R{}^2}{2\mu} + \frac{J^2}{2\mu R^2} + V^{\mathrm{AC}}(R,\xi_{\mathrm{AC}}) \tag{9}$$

Since the Hamiltonian in eq 9 includes two dynamical variables (p_R and R), the capture probability and cross section can be calculated analytically

$$\bar{S}^{\mathrm{AC}}(E) = \int_0^1 S^{\mathrm{AC}}(E,\xi_{\mathrm{AC}})\,\mathrm{d}\xi_{\mathrm{AC}}$$

$$S^{\mathrm{AC}}(E,\xi_{\mathrm{AC}}) = \frac{\pi J_{\mathrm{m}}{}^2(E,\xi_{\mathrm{AC}})}{2\mu E}$$

$$P^{\mathrm{AC}}(E,J,\xi_{\mathrm{AC}}) = \Theta\lfloor E - \max(J^2/2\mu R^2 + V^{\mathrm{ACPR}}(R,\xi_{\mathrm{AC}}))\rfloor \quad (10)$$

where $J_{\mathrm{m}}(E,\xi_{\mathrm{AC}})$ is the maximal angular momentum that yields nonzero probability expressed through the Θ step function and E is the collision energy. Note that, in distinction to eq 4, ξ_{AC} in eq 10 is not the cosine of an initial orientation angle but that of an orientation angle in the region where the intrinsic angular momentum j is "locked" to the collision axis. To get the partial AC cross section as a function of the initial orientation ξ_i, $\tilde{S}^{\mathrm{AC}}(E,\xi_i)$, one should transform $S^{\mathrm{AC}}(E,\xi_{\mathrm{AC}})$ by way of locking probability $\prod(\xi_i,\xi_{\mathrm{AC}},E)$

$$\tilde{S}^{\mathrm{AC}}(E,\xi_i) = \int_0^1 \prod(\xi_i,\xi_{\mathrm{AC}},E) S^{\mathrm{AC}}(E,\xi_{\mathrm{AC}})\,\mathrm{d}\xi_{\mathrm{AC}} \quad (11)$$

Here, $\prod(\xi_i,\xi_{\mathrm{AC}},E)$ is the probability of the population redistribution from the bunch of states with the same $p_\phi/j = \xi_{\mathrm{AC}}$ (but differing in angles ϕ) in the region of the locked intrinsic momentum to the bunch of states with $p_\phi/j = \xi_i$ (again differing in angles ϕ) in the region of free intrinsic momentum. The calculation of the probability $\prod(\xi_i,\xi_{\mathrm{AC}},E)$ should be based on the RA Hamiltonian applied only to the incoming part of the collision, from the asymptotic region to the region of locking. If the latter is well defined, the function $\prod(\xi_i,\xi_{\mathrm{AC}},E)$ can be unambiguously determined and normalized to unity, $\int_0^1 \prod(\xi_i,\xi_{\mathrm{AC}},E)\,\mathrm{d}\xi_i = 1$. Otherwise, the transformation expressed in eq 11 does not exist. Assuming that $\prod(\xi_i,\xi_{\mathrm{AC}},E)$ exists, one gets the relation

$$\int_0^1 \tilde{S}^{\mathrm{AC}}(E,\xi_i)\,\mathrm{d}\xi_i = \int_0^1 S^{\mathrm{AC}}(E,\xi_{\mathrm{AC}})\,\mathrm{d}\xi_{\mathrm{AC}} \quad (12)$$

In other words, the possibility of replacing the averaging over the initial orientation angles by the averaging over the orientation angles of the locked intrinsic momentum constitutes an additional assumption of the AC approximation, which was not spelled out in the initial formulation of the AC model.[9,10]

Another property that follows from the existence of the probability function $\prod(\xi_i,\xi_{\mathrm{AC}},E)$ is the relation between the AC and RA cross sections (see eq 6)

$$\bar{S}^{\mathrm{AC}}(E) = \lim_{j \ll \ell} \bar{S}^{\mathrm{RA}}(E,j) \quad (13)$$

Equation 13 relates the conventional AC cross sections $S^{\mathrm{AC}}(E)$ to RA cross sections $\bar{S}^{\mathrm{RA}}(E,j)$ provided that the function $\prod(\xi_i,\xi_{\mathrm{AC}},E)$ exists.

FW Hamiltonian and Cross Sections. The FW Hamiltonian is obtained from the RA Hamiltonian in eq 2 taking β as an angular coordinate and expressing ℓ^2 through the momentum p_β conjugate to polar angle β and yet another momentum p_δ conjugate to the azimuthal angle δ

$$H^{\mathrm{FW}}(p_R,R,p_\beta,\beta;p_\delta) = \frac{p_R{}^2}{2\mu} + \frac{1}{2\mu_R{}^2}\left(p_\beta{}^2 + \frac{p_\delta{}^2}{\sin^2\beta}\right) + V^{\mathrm{AC}}(R,\cos\beta) \quad (14)$$

where p_δ is the conserved projection of the (nonconserved) angular momentum vector $\mathbf{l}$ onto the z-axis. The mean capture cross section $\bar{S}^{\mathrm{FW}}$ can be calculated as the ratio of the microcanonical "captured" flux through a sphere of a large radius to the collision velocity and to the density of states in the momentum space. Simple derivation, which basically repeats that in ref 24, leads to the following expression for $\bar{S}^{\mathrm{FW}}$

$$\bar{S}^{\mathrm{FW}}(E) = \frac{1}{8\pi\mu E}\int_{\mathrm{capt}} \mathrm{d}p_{\beta_{\mathrm{i}}}\,\mathrm{d}\beta_{\mathrm{i}}\,\mathrm{d}p_{\delta_{\mathrm{i}}}\,\mathrm{d}\delta_{\mathrm{i}} \quad (15)$$

where the integration over the indicated variables corresponds to the initial conditions (subscript i) of those trajectories that get captured. Under the condition in eq 7, the FW cross sections are expected to be related to the RA cross sections as

$$\bar{S}^{\mathrm{FW}}(E) = \lim_{j \gg \ell} \bar{S}^{\mathrm{RA}}(E,j) \quad (16)$$

Note that neither the AC cross section nor the FW cross section depend on j. Finally, we remark that the Hamiltonian in eq 14 contains four dynamical variables (p_R,R,p_β,β) and therefore trajectory calculations can be performed only numerically. The reason FW approximation requires more effort, compared to AC approximation, for calculation of the mean cross sections is that the latter circumvents the calculation of the redistribution function $\prod$ by simply assuming that it exists.

4. Capture for Charge−Quadrupole Interaction

The leading interaction terms for the ion−neutral diatom system at low collision energies are the anisotropic charge−quadrupole (cq) potential and isotropic charge-induced dipole (Langevin) potentials. Since the former is proportional to $1/R^3$, and the latter to $1/R^4$, the cq potential is expected to determine the capture rate coefficients at low enough temperatures. We therefore first consider the pure charge−quadrupole interaction and then calculate, in section 5, the correction to the rate constant which is due to the charge-induced dipole interaction. A small value of this correction would indicate that other possible terms, which could originate from a full potential energy surface, are negligible.

The charge−quadrupole potential reads

$$U_{\mathrm{cq}}(R,\gamma) = \frac{qQ}{R^3}P_2(\cos\gamma) \quad (17)$$

where q is the charge of the ion, Q is the quadrupole moment of the diatom and $P_2(\cos\gamma) = (3\cos^2\gamma - 1)/2$ is the Legendre polynomial. The potential in eq 17 generate the following AC potentials

$$V^{\mathrm{AC}}(R,\cos\beta) = -\frac{qQ}{2R^3}P_2(\cos\beta) \quad (18)$$

The Hamiltonian in eq 2 with potential from eq 18 can be brought to the dimensionless form. Using the Greek characters for reduced dynamical variables and parameters, we write

$$\rho = (E^{1/3}|qQ|^{-1/3}) \times R, \quad \pi_\rho = (E^{-1/2}\mu^{-1/2}) \times p_R$$

$$(I,\iota,\pi_\phi,\pi_\beta,\pi_\delta) = (E^{-1/6}\mu^{-1/2}|qQ|^{-1/3}) \times (J,j,p_\phi,p_\beta,p_\delta)$$

$$\tau = (E^{5/6}\mu^{-1/2}|qQ|^{-1/3}) \times t, \quad \epsilon = (E^{-1}) \times E = 1 \quad (19)$$

The dimensionless Hamiltonians $\eta_{\mathrm{cq}}^{\mathrm{RA,s}} = H_{\mathrm{cq}}^{\mathrm{RA,s}}/E$ expressed in terms of two dimensionless coordinates ρ and ϕ and their

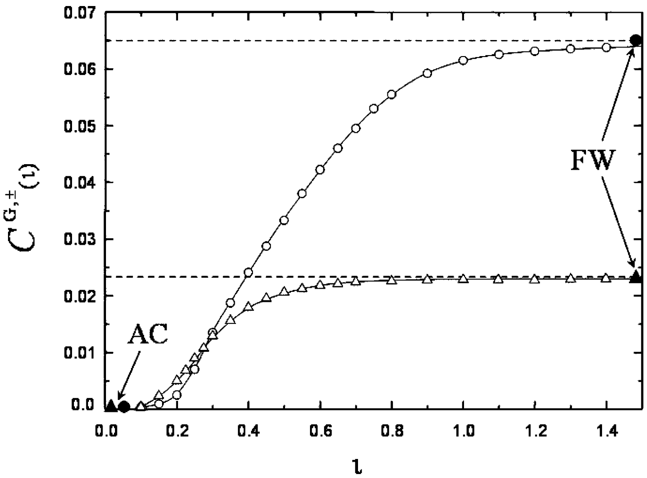

Figure 1. Fractional gyroscopic corrections $C^{G,\pm}(\iota)$ to the classical AC cq capture cross sections vs reduced angular momentum of the diatom. Open circles correspond to $s = +$ and open triangles to $s = -$. Filled symbols correspond to AC and FW approximations.

two conjugate action variables π_ρ and π_ϕ assume the form

$$\eta_{cq}^{RA,s}(\pi_\rho,\rho,\pi_\phi,\phi;I,\iota) = \frac{\pi_\rho^{\ 2}}{2} + \frac{I^2 + \iota^2 - 2\pi_\phi^{\ 2} - 2\sqrt{I^2 - \pi_\phi^{\ 2}}\sqrt{\iota^2 - \pi_\phi^{\ 2}}\cos\phi}{2\rho^2} - s\,\frac{3(\pi_\phi/\iota)^2 - 1}{4\rho^3} \quad (20)$$

where $s = \pm 1$ arises from the sign of the product qQ. Similarly, the reduced FW and AC Hamiltonians are

$$\eta_{cq}^{FW,s}(\pi_\rho,\rho,\pi_\beta,\beta;I,\pi_\delta) = \frac{\pi_\rho^{\ 2}}{2} + \frac{1}{2\rho^2}\left(\pi_\beta^{\ 2} + \frac{\pi_\delta^{\ 2}}{\sin^2\beta}\right) - s\frac{3\cos^2\beta - 1}{4\rho^3} \quad (21)$$

and

$$\eta_{cq}^{AC,s}(\pi_\rho,\rho;I,\xi_{AC}) = \frac{\pi_\rho^{\ 2}}{2} + \frac{I^2}{2\rho^2} - s\,\frac{3\xi_{AC}^{\ 2} - 1}{4\rho^3} \quad (22)$$

The above reduced Hamiltonians generate capture trajectories for a single reduced collision energy $\epsilon = 1$.

For the AC approximation, the mean capture cross sections $\bar{s}_{cq}^{AC,s}$ are calculated analytically and are certain numbers

$$\bar{s}_{cq}^{AC,s} = \frac{3\pi}{4}\int_0^1 [s(3\xi_{AC}^{\ 2} - 1)]^{2/3}\Theta(s(3\xi_{AC}^{\ 2} - 1))\,d\xi_{AC}$$

$$\bar{s}_{cq}^{AC,+} = 1.249$$

$$\bar{s}_{cq}^{AC,-} = 1.422 \quad (23)$$

The cross sections for FW Hamiltonian and RA Hamiltonians are calculated numerically by integration of an equation of motion with the systematic variation of initial conditions; the latter allows one to avoid statistical errors inherent in the Monte Carlo method. The results of calculations of $\bar{s}_{cq}^{RA,s}$ are summarized as two plots of gyroscopic corrections $C^{G,\pm}(\iota)$ in the following expression for $\bar{s}_{cq}^{RA,s}(\iota)$ (see Figure 1)

$$\bar{s}_{cq}^{RA,s}(\iota) = \bar{s}_{cq}^{AC,s} \times (1 + C^{G,s}(\iota)) \quad (24)$$

We see that the gyroscopic effect in the mean capture cross section $\bar{s}_{cq}^{RA,s}(\iota)$ is not very large. We also see that RA cross sections exceed the AC ones and tend, for $\iota \gg 1$, to FW cross sections. We ascribe the former feature to the fact that the RA Hamiltonian takes into account a mutual adjustment of the collision axes and the angular momentum vector, while no such adjustment occurs within the AC approximation. Since the RA approximation takes into account the Coriolis (i.e., nonadiabatic) effects with respect to the projection of j onto the collision axis, we can say that neglect of this kind of nonadiabatic coupling underestimates the cross sections for the energy range studied (low collision energies). This is different from nonadiabatic effects at higher collisions energies, where neglecting nonadiabatic coupling overestimates the cross sections.[25] The final remark refers to the reason the gyroscopic effect in the mean capture cross section is not very pronounced. This might be related to the fact that in the averaging procedure over all the projections of j onto the collision axis in the configurations, which are mainly responsible for capture, the direction of the quantization axis (be it SF or BF axes for FW or AC approximations, respectively) does not matter much since in traversing this configuration the projections of j onto the collision axis presumably do not change a lot. A similar conclusion, but in a different context, was reached in ref 26, where it was found, for the potential in eq 17, that the infinite order sudden (IOS) approximation yields the capture cross sections which are not very different from the capture cross sections in the sudden (S) approximation. The IOS approximation is a counterpart of the AC approximation, while the S approximation is a counterpart of the FW approximation; the difference between them is that in the AC and FW approximations the angle variable is β (the angle between the collision axis and the intrinsic angular momentum, eq 18) while in the IOS and S approximations the angle variable is γ (the angle between the collision axis and the axis of the diatom, eq 17). Of course, the absolute values of the cross sections for AC/FW and IOS/S approximations are quite different.

We now dwell on the partial capture cross sections which are associated with certain initial values of the projection, ξ_i, and which for the RA, FW, and AC Hamiltonians in eq 20−22 are $s_{cq}^{RA,s}(\iota,\xi_i)$, $s_{cq}^{FW,s}(\xi_i)$, and $s_{cq}^{AC,s}(\xi_{AC})$, respectively. The AC cross section can be expressed analytically as

$$s_{cq}^{AC,s}(\xi_{AC}) = \frac{3\pi}{4}[s(3\xi_{AC}^{\ 2} - 1)]^{2/3}\Theta(s(3\xi_{AC}^{\ 2} - 1)) \quad (25)$$

where the step Θ function excludes the channels that are classically closed for capture. The capture cross sections for the RA and FW Hamiltonians require numerical analyses of the capture trajectories. Some results of the analysis are presented by four plots $s_{cq}^{RA,s}(\iota,\xi_i)_{i=0.1}$, $s_{cq}^{RA,s}(\iota,\xi_i)_{i=0.25}$, $s_{cq}^{FW,s}(\xi_i)$ vs ξ_i, and $s_{cq}^{AC,s}(\xi_{AC})$ vs ξ_{AC} in Figures 2 and 3. The cross sections $s_{cq}^{AC,\pm}(\cos\beta_{AC})$ are given by analytical formulas (eq 25) with the vanishing portions of the graphs corresponding to the initial conditions for which capture is not possible, that is, $\xi_{AC}^{+} < (1/3)^{1/2}$ and $\xi_{AC}^{-} > (1/3)^{1/2}$ for $s = +$ and $s = -$, respectively. The "forbidden" range is also seen in $s_{cq}^{RA,\pm}(\iota,\xi_i)_{i=0.1}$ and $s_{cq}^{RA,\pm}(\iota,\xi_i)_{i=0.25}$ with a larger extension for a smaller value of ι. This is consistent with the condition in eq 6, implying that, with a decrease in ι, the AC approximation performs progressively better. We also see that even $\iota = 0.1$ notably differs from $s_{cq}^{AC,+}(\xi_{AC})$; nonetheless, this difference

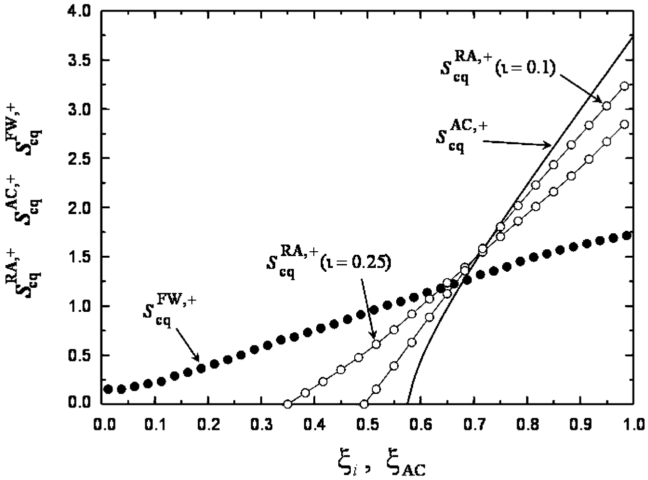

Figure 2. Reduced partial capture cq cross sections vs the fractional projections of intrinsic angular momentum ξ_i,ξ_{AC} for $s = +$. The full curve stands for analytical $s_{cq}^{AC,+}(\xi_{AC})$, open circles connected by lines for numerical $s_{cq}^{RA,+}(\xi_i)_{\iota=0.1}$ and $s_{cq}^{RA,+}(\xi_i)_{\iota=0.25}$, and filled circles for $s_{cq}^{FW,+}(\xi_i)$.

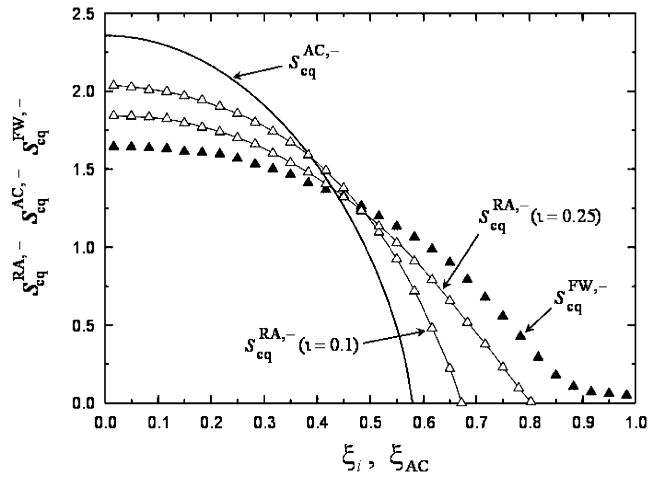

Figure 3. Same as Figure 2 for $s = -$, with circles replaced by triangles.

does not mar the main assumption of the AC approach: the conservation of the projection of **j** onto the collision axis. It should be noted that the $1/R^3$ anisotropic interaction is the optimum one for probing this basic AC assumption, since the onset of interaction is vary gradual and the reorientation of the **j** vector from the space-fixed axis to the body-fixed axis occurs with minimal nonadiabatic effects.

Yet another interesting observation refers to the fact that the plots $s_{cq}^{RA,+}(\iota,\xi_i)_{\iota=0.1}$ and $s_{cq}^{RA,+}(\iota,\xi_i)_{\iota=0.25}$ are closer to $s_{cq}^{AC,s}(\xi_{AC})$ than $s_{cq}^{RA,-}(\iota,\xi_i)_{\iota=0.1}$ and $s_{cq}{}^{RA,-}(\iota,\xi_i)_{\iota=0.25}$ to $s_{cq}^{AC,-}(\xi_{AC})$. This is consistent with the condition that the precession frequencies in the region of capture are higher in the $s = +$ case, that is, the AC approximation performs better for this case.

With an increase in ι, the AC approximation performs worse which is manifested in the shrinking of the forbidden range of cos β as a result of the increasing Coriolis interaction and opening of the capture channels. Finally, in the FW limit, the gyroscopic effect is maximal. It is interesting that $s_{cq}^{FW,\pm}$ has no vanishing portions and is nonzero for $\xi_i^+ = 0$ and $\xi_i^- = 1$, respectively. This is explained by the fact that the diatom, say for the $s = +$ case, with its angular momentum vector directed normally to the velocity vector **v** ($\xi_i^+ = 0$) and conserved throughout the collision, will enter the interaction region with a nonzero projection of **j** onto **R**. If this projection (i.e., $\cos^2 \beta$ in the potential of the FW Hamiltonian, see eq 21) at a proper time moment turns out to be large enough to make the potential attractive, then the colliding pair will see an effective potential barrier (made up of an attractive cq interaction and centrifugal repulsion). Occasional crossing of this barrier results in the capture. The interplay of these rather complicated events is responsible for a finite value of the capture cross section for ξ_i^+ in the FW limit. More details of the capture dynamics can be inferred from the behavior of the individual trajectories near the separarix that determines the capture region in the system phase space. The respective material can be obtained from the authors by request.

5. Discussion

Since the gyroscopic effect does not change the AC mean capture cross sections in a very pronounced way, one should consider also other reasons that could affect the charge–quadrupole AC cross sections. There are two of them: quantization of the intrinsic angular momentum and the influence of the isotropic charge-induced dipole (called also Langevin, L) interaction of the form $U_L(R) = -\alpha q^2/2R^4$. The former is essential only for not too large values of the rotational quantum numbers of the diatom and the latter for not too small values of the collision energy. In the spirit of the perturbation approach, each correction can be found by proper generalization of the fully classical AC Hamiltonian η_{cq}^{AC}, eq 22.

The quantum correction for the diatom rotation is calculated from the AC quantum (with respect to rotor) Hamiltonian η_{cq}^{QAC} in which the cq potential energy is written through the rotational quantum number j and the projection quantum number ω (beginning here, j and ω mean the quantum numbers that correspond to the dynamical variables of the intrinsic angular momentum and its projection onto the collision axis)

$$\eta_{cq}^{QAC,s}(\pi_\rho,\rho;I,j,\omega) = \frac{\pi_\rho^{\ 2}}{2} + \frac{I^2}{2\rho^2} - s\,\frac{3\omega^2 - j(j+1)}{(2j-1)(2j+3)\rho^3} \tag{26}$$

Then, the standard QAC calculations with cq potential yield

$$\bar{s}_{j,cq}^{QAC} = \bar{s}_{cq}^{AC} \times (1 + C_j^Q) \tag{27}$$

where

$$C_j^Q = \frac{\dfrac{1}{2j+1}\displaystyle\sum_{\tilde{\omega}=-\tilde{j}}^{\tilde{\omega}=\tilde{j}}\left[s\,\frac{3\omega^2 - j(j+1)}{(2j-1)(2j+3)}\right]^{2/3}\Theta[s(3\omega^2 - j(j+1))]}{2^{4/3}\displaystyle\int_0^1 [s(3x^2-1)]^{2/3}\Theta(s(3x^2-1))} - 1 \tag{28}$$

Quantum correction coefficients C_j^Q are plotted in Figure 4 for $j \geq 2$.

The Langevin correction can be found from the AC classical Hamiltonian supplemented with the charge-induced dipole interaction

$$\eta_{cqL}^{AC,s}(\pi_\rho,\rho;I,\xi_{AC},\lambda) = \frac{\pi_\rho^{\ 2}}{2} + \frac{I^2}{2\rho^2} - s\,\frac{3\xi_{AC}^{\ 2} - 1}{4\rho^3} - \lambda\,\frac{1}{2\rho^4} \tag{29}$$

where a parameter in front of the scaled Langevin interaction is $\lambda = \alpha|q/Q^2|^{2/3} E^{1/3}$ with α being the polarizability of the

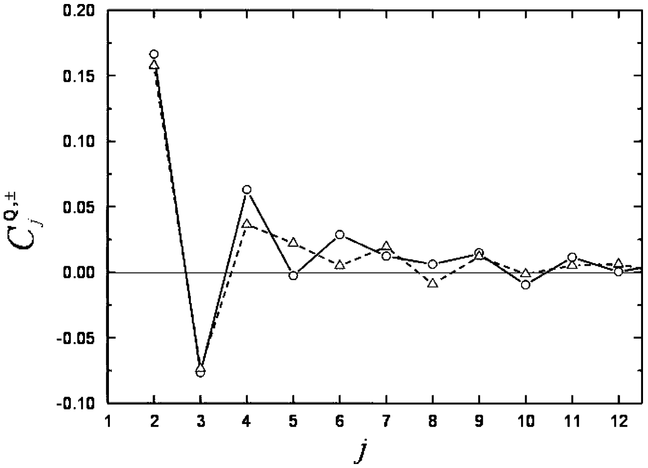

Figure 4. Fractional quantum corrections $C_j^{Q,\pm}$ to the classical AC cq capture cross sections vs angular momentum quantum number of the diatom. Open circles correspond to $s = +$ and open triangles to $s = -$.

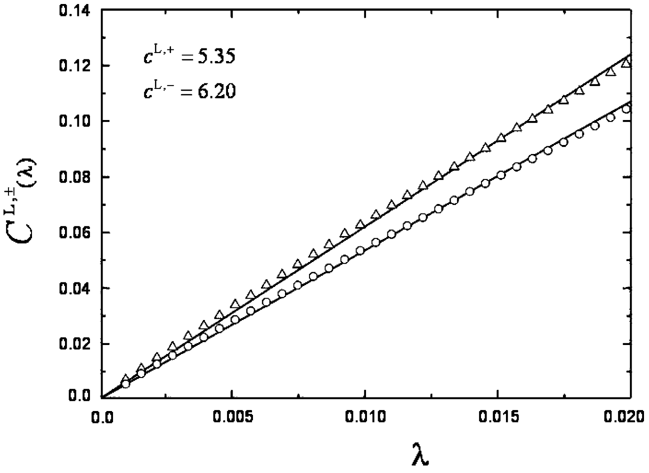

Figure 5. Fractional Langevin corrections $C_j^{L,\pm}(\lambda)$ to the classical AC cq capture cross sections vs the reduced strength of the Langevin interaction λ. Open circles correspond to $s = +$ and open triangles to $s = -$; full lines represent the linear fit to numerical results with the slope coefficients $c^{L,+} = 5.35$ and $c^{L,-} = 6.20$.

diatom. The calculation of captured trajectories for the AC Hamiltonian in eq 29 is easy, especially so when one adopts the parametric description of the capture.[28] For small values of λ, the Langevin correction $C^{L,s}(\lambda)$ to the cq cross section is expected to be roughly linear in λ (see Appendix B), so that

$$\bar{s}_{cq}^{LAC,s} = \bar{s}_{cq}^{\ AC,s} \times (1 + C^{L,s}(\lambda))$$

$$C^{L,s}(\lambda) = c^{L,s}\lambda \tag{30}$$

The quality of linear approximation and the values of the coefficients $c^{L,\pm}$ are presented in Figure 5.

Collecting all the corrections to the fully classical AC capture cross section for the PR charge−quadrupole interaction, we arrive at the following expression for the rotationally adiabatic state-selected quantum-classical capture cross section that includes the effect of quantization of the intrinsic angular momentum, gyroscopic effect, and weak manifestation of the Langevin interaction

$$\bar{s}_{j,cqL}^{QRA,s}(\iota,\lambda) = \bar{s}_{cq}^{\ AC,s}(1 + C_j^{Q,s} + C^{G,s}(\iota) + C^{L,s}(\lambda)) \tag{31}$$

Here, $\bar{s}_{cq}^{AC,\pm}$ are numbers (see eq 24), and each correction depends on its dimensionless variable (either intrinsic rotational quantum number j, reduced intrinsic angular momentum ι, or the strength of the Langevin interaction λ).

TABLE 1: Values of $\bar{\ell}/\hbar$ and $c^{L,-}\bar{\lambda}$ at Different Temperatures for the Capture of N_2 by a Heavy Positive Ion

T/K	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}
$\bar{\ell}/\hbar$	2.8	4.1	6.1	8.9	13.1
$c^{L,-}\bar{\lambda}$	0.01	0.02	0.05	0.1	0.24

Dimensionless cross sections s can be translated into the energy-dependent cross sections $\bar{S}$, temperature-dependent cross sections $\langle S \rangle$, and rate coefficients K in conventional units

$$\bar{S}_{cq}^{AC,\pm}(E) = B^{\pm}(|qQ|/E)^{2/3}$$

$$\bar{S}_{j,cqL}^{QRA,\pm}(E,\iota,\lambda) = \bar{S}_{cq}^{AC,\pm}(E)(1 + C_j^{Q,s} + C^{G,s}(\iota) + C^{L,s}(\lambda)) \tag{32}$$

$$\langle S_{cq}^{AC,\pm}(T) \rangle = \int \bar{S}_{cq}^{AC,\pm}(E) \exp(-E/kT)E \, dE/(kT)^2 = C^{\pm}(|qQ|/kT)^{2/3}$$

$$K_{j,cqL}^{QRA,\pm}(T) = \sqrt{8kT/\pi\mu} \times \langle S_{cq}^{AC,\pm}(T) \rangle \times (1 + C_j^{Q,\pm} + \bar{C}^{G,\pm}(\iota) + \bar{C}^{L,\pm}(\bar{\lambda})) \tag{33}$$

where the numerical factors $B^{\pm}$ and $C^{\pm}$ are $B^{+} = 0.883$, $B^{-} = 1.006$, $C^{+} = 0.789$, and $C^{-} = 0.898$. Here, $\bar{C}^{G,\pm}(\tilde{\iota})$ and $\bar{C}^{L,\pm}(\bar{\lambda})$ are the functions which are obtained in the thermal averaging of $C^{G,\pm}(\iota)$ and $C^{L,\pm}(\lambda)$ and which depend on parameters $\bar{\iota}$ and $\bar{\lambda}$. The latter are defined as

$$\bar{\iota} = \hbar(j + {}^{1}/_{2})(kT)^{-1/6}\mu^{-1/2}|qQ|^{-1/3}$$

$$\bar{\lambda} = \alpha|q/Q^2|^{2/3}(kT)^{1/3} \tag{34}$$

Since the energy dependence of parameters ι and λ is very weak, the averaging introduces but minute changes into the functions $C^{G,\pm}(\iota)$ and $C^{L,\pm}(\lambda)$, and one can simply put $\bar{C}^{G,\pm}(\bar{\iota}) = C^{G,\pm}(\bar{\iota})$ and $\bar{C}^{L,\pm}(\bar{\lambda}) = C^{L,\pm}(\bar{\lambda})$ and use the graphs in Figures 1, 4, and 5 for estimating the corrections in eq 31. Note that with a decrease in temperature and fixed value of j, the gyroscopic correction increases and Langevin correction decreases. On the other hand, with a decrease in j at a fixed temperature, the quantum correction increases and the gyroscopic correction decreases.

Equations 32, 33, and 34, together with Figures 1, 4, and 5 summarize the results of this study. They are valid under two restrictive conditions: the weak effect of the Langevin interaction and the condition of classical capture. The first condition is not essential since, when the Langevin correction becomes higher than the gyroscopic one, the latter can be neglected and the resulting AC rate coefficient matches with the ACCl rate coefficients for more general types of interactions (Langevin plus higher-order charge−dipole intetractions).[28] The second condition, $\bar{\ell} \gg \hbar$, defines the lower temperature limit, above which the capture event can be described classically. From Table 1, appropriate for N_2 + heavy ion collisions, we see that this temperature limit is about 10^{-5} K, and by comparison with Figure 1, we infer that at this temperature the gyroscopic correction can be larger than the Langevin one.

Conclusion

This study falls into the category of works devoted to analysis of trajectories in the classical capture for systems with two degrees of freedom. Earlier papers addressed the planar capture for the ion−anisotropically polarizable (anisotropic Langevin) diatom interaction,[29,30] ion−dipolar diatom interaction,[31] and the anisotropic Langevin interaction supplemented with a short-range repulsion.[32,33] The parameter space of the models studied was not very wide which allowed one to get some analytical insight into the problem. Our paper addresses three-dimensional capture for the charge−quadrupole (cq) interaction under the additional assumption of adiabatic conditions with respect to transitions between rotational states of the diatom. In this respect, this paper is complimentary to the earlier ones.[28−33] The final expression for the capture rate constant contains, besides the trivial factor (qQ/k_BT), three dimensionless parameters: the rotational quantum number of the diatom (in the quantum correction to the classical cq AC rate coefficient), the reduced intrinsic momentum (in the gyroscopic correction to the cq AC rate coefficient), and the reduced strength of the isotropic Langevin interaction (in the Langevin correction to the cq AC rate coefficient). The assumption about the PR approximation, adopted in this paper, can be relaxed within the same formalism, provided that one is prepared to introduce one more parameter, which will include the rotational constant of the diatom. However, the deviations from the cq PR approximation will show up at higher collision energies, when the gyroscopic correction is expected to be small. This is the reason we kept the PR approximation in addressing our main goal: gyroscopic effect in the capture.

In the capture of a rotating diatomic molecule by an ion, the gyroscopic property of the former leads to the decoupling of the intrinsic angular momentum from the collision axis. This decoupling, which is ignored within the AC treatment of the capture, is studied in this paper for classical low-energy (low-temperature) collisions that proceed adiabatically with respect to rotational transitions in the diatomic partner and that are governed mainly by the first-order charge−quadrupole interaction (PR approximation). The gyroscopic effect manifests itself in the increase of the ACPR cross sections that tend, for large enough intrinsic momenta j, to the cross sections calculated in the FW approximation when j is assumed to conserve its orientation in space. The effect of the Coriolis interaction in the mean classical capture cross sections is much weaker than its quantum counterpart[13] for the capture in the quantum regime. This can be explained by the higher sensitivity of the capture dynamics at ultralow energies to the interaction potentials and the Coriolis coupling. Indeed, the gyroscopic effect is responsible for pure attractive character of the lowest axially nonadiabatic potential that determines the zero-temperature capture rate coefficient. On the other hand, rather weak dependence of the classical capture rate coefficient on j parallels that of the zero-temperature limit of the rate coefficient. Finally, we note that since the classical description of capture is valid already for $\bar{\ell}$ values of about several units of $\hbar$,[27] the condition $j \approx \bar{\ell}/\hbar$ is quite compatible with experimental possibilities for studying the capture of rotationally excited diatoms at very low collision energies.

Regarding the results obtained from a more practical point of view, we note that, if the inaccuracy in the capture cross sections of about 5−10% can be tolerated, one can still use the ACPR approach for calculating the low-energy mean capture cross sections for rotationally excited diatoms by an ion, even beyond its formal condition of applicability, which requires the fast precession of the intrinsic angular momentum about the collision axis on the time scale of a collision. This conclusion, however, does not hold for the partial capture cross sections that characterize the capture of rotationally polarized diatoms.

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Appendix A. Glossary of Super- and Subscripts

AC:	Adiabatic channel, fully classical (Hamiltonian, cross sections, and rate coefficients)
cq:	charge−quadrupole (interaction, cross sections, and rate coefficients)
FW:	Flywheel (Hamiltonian, cross sections, and rate coefficients)
G:	Gyroscopic (effect, correction)
L:	Langevin (interaction, correction)
PR:	Perturbed-rotor (potential, Hamiltonian)
QAC:	Adiabatic channel, with quantal rotation and classical relative motion (Hamiltonian, cross sections, and rate coefficients)
RA:	Rotationally adiabatic (Hamiltonian, cross sections, and rate coefficients)

Appendix B. Langevin Correction to the Charge−Quadrupole Capture Cross Section

A rough λ-dependence of the Langevin correction to the charge−quadrupole capture cross sections for the Hamiltonian in eq 29 can be found from the following considerations. The cq cross section is obtained as the average of β-dependent partial cross sections. The latter vanish at $\cos^2 \beta = {}^1\!/_3$, and the major contribution to the Langevin correction in the classical capture cross section for the Hamiltonian in eq 29 comes from those values of $\cos \beta$ at which the cq potential nearly vanishes. Defining the angular range of a very weak cq potential through $\Delta\beta$ around $\cos \beta_0 = (1/3)^{1/2}$, we write the correction as $S_L\Delta\beta$ where S_L is the Langevin cross section, $S_L \propto (q^2\alpha/E)^{1/2}$. The value of $\Delta\beta$ can be estimated from the condition that the increment in the cq potential $\Delta\beta/\rho^3$ is of the order of the Langevin potential λ/ρ^4 at the Langevin capture distance $\rho \approx \rho_L \propto (\lambda)^{1/2}$. In this way, the Langevin correction to the cq cross section will be proportional to $S_L\Delta\beta \propto S_L(\lambda)^{1/2} \propto (q^2\alpha/E)^{1/2}\alpha^{1/2}|q/Q^2|^{1/3}E^{1/6}$. The relative correction to the cq cross section C^L is then calculated as $C^L \propto S_L\Delta B/S_{cq}^{AC} \approx (E/|qQ|)^{2/3}S_L\Delta\beta \propto \lambda$, that is, $C^L(\lambda) = c^L\lambda$ irrespective of s. In reality, the functions $C^{L,s}(\lambda)$, calculated numerically, are weakly nonlinear and are characterized by slightly different linear fitting coefficients $c^{L,\pm}$; see Figure 5.

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