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Spin-rotation interaction in cold and ultracold collisions of $N_2^+(^2\Sigma^+)$ with ^{3}He and ^{4}He

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In a recent work we compared spin-free collisions of N_2^+ with ^{3}He and ^{4}He using a newly developed potential energy surface. We found that such collisions exhibit a strong isotope effect in the ultracold regime. In the present study we consider the role of the spin-rotation interaction in cold He-N_2^+ collisions. We find that our spin-free vibrational quenching cross sections are not affected. Conversely, the cross sections for rotational quenching are strongly modified in the ultracold regime and exhibit resonance structures which are analyzed. These structures, which are not observed when the spin-rotation interaction is omitted, are shown to be due to the Feshbach resonances associated with the nonconservation of parity.

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I. INTRODUCTION

Many theoretical studies [1–4] in the field of the production of ultracold molecules are devoted to the understanding of collisional energy transfer, as it is required to optimize the experimental cooling and trapping techniques of neutral [5,6] or ionic species [7,8], and to choosing the best candidates. For many of these atom-diatom collisions, the probability of collisional energy transfer is very large at temperatures near zero kelvin, and small perturbations of the potential in this range of temperature may suppress or create new resonance patterns. One example of such an effect is the spin-rotation interaction, whose magnitude is comparable to collision energies in cold collisions involving a $^2\Sigma$ diatomic molecule. This effect, which is presently being considered by several theoretical teams [9,10], was first studied only recently in the ultracold regime by Balakrishnan *et al.* for the ^{3}He-CaH collision [11]. They found that the spin-rotation interaction is strong enough for this system to produce new resonances and to suppress the rotational relaxation of the negative-parity state in the Wigner regime. They also concluded that spin-rotation effects were negligible for vibrational deactivation of CaH in collision with He.

In a recent work [12] we compared spin-free collisions of $N_2^+(^2\Sigma^+)$ with ^{3}He and ^{4}He using a newly developed potential energy surface. We found that the vibrational deactivation of N_2^+ $(\nu=1,j=0)$ exhibits a strong isotope effect in the ultracold regime. The starting point of the present work was to check that our results are unchanged when the spin-rotation interaction is included and then to study the effect of spin rotation on rotational quenching. This is to our knowledge the first study including spin rotation for a collision involving an ionic $^2\Sigma^+$ diatomic molecule. Spin-orbit and orbit-rotation terms in the total molecular Hamiltonian should also be considered as they mix $^2\Sigma$ and $^2\Pi$ electronic states. However, in the case of N_2^+, the $^2\Pi$ state is more than 1 eV higher in energy than the $^2\Sigma$ state. Consequently, it can be neglected in the very low collision energy regime. The spin-rotation constant of N_2^+ $(\gamma=8.3\times10^{-3}\text{ cm}^{-1})$ [13] is five times smaller than that of CaH $(\gamma=4.5\times10^{-2}\text{ cm}^{-1})$, and the rotational level splittings of N_2^+ due to the spin-rotation interaction are smaller than those of CaH. However, they are still comparable to ultracold collision energies. On the other hand, the rotational constant of N_2^+ $(Be=1.93\text{ cm}^{-1})$ is a factor of 2 smaller than that of CaH $(Be=4.27\text{ cm}^{-1})$, so the ratio Be/γ of N_2^+ is approximately twice as large as for CaH. We will see that the strong spin-rotation interaction cannot be neglected in calculations of rotational quenching in the ultracold regime as the spin-rotation interaction yields new resonance structures which are not observed in the spin-free results.

The paper is organized as follows. In Sec. II we briefly recall the main steps of the close-coupling calculations in a coupled representation, including the spin-rotation interaction, which we coded, and give the calculation parameters. The results of the calculations are presented and discussed in Sec. III.

II. CALCULATIONS

As the quantum scattering theory of collisions between diatomic molecules in the $^2\Sigma^+$ electronic state and structureless targets was developed and described in detail in the early work of Alexander [14,15] and Corey and McCourt [16] we will only define a few notations which will be used later and specify the differences between the present study and previous work. Our approach is different from that of Balakrishnan *et al.* [11] in that we perform calculations in the space-fixed basis set and use a coupled representation of the wave function built from definite-parity (ε) Hund's case (a) functions for the $^2\Sigma^+$ diatomic molecule introduced by Zare *et al.* [17], as recommended by Alexander. In what follows N and $j=N-\varepsilon/2$ will designate the total angular momentum quantum number of the diatomic molecule excluding and including spin, respectively. The spin-dependent energies of the diatomic molecule can be written as

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$$E_{N\varepsilon} = E_N - \frac{\varepsilon}{2}\gamma\left(N + \frac{(1+\varepsilon)}{2}\right). \tag{1}$$

The spin-free energies E_N are obtained by solving the diatomic equation without the spin-rotation coupling term following the standard procedure detailed in our previous paper devoted to N_2^+ [12]. The presence of the electronic spin in a $^2\Sigma^+$ state acts to split the rotational levels into doublets with a spacing which increases linearly with N,

$$E_{N,\varepsilon=-1} - E_{N,\varepsilon=1} = \left(N + \frac{1}{2}\right)\gamma. \tag{2}$$

The sign of γ is positive for N_2^+ as it is for CaH, which means that the positive-parity levels are the lowest inside a doublet. In what follows we will compare our results with those obtained from spin-free close-coupling calculations. These calculations are also performed in the space-fixed reference frame using our code which was described in previous publications [18].

The same three-dimensional potential energy surface is used to perform the calculations as in our previous papers devoted to He-N_2^+ [19]. This surface is based on a large grid of *ab initio* points calculated at the multireference configuration interaction level using an augmented correlation-consistent polarization valence quadruple zeta (aug-cc-pVQZ) basis set [20]. The analytical model of the potential energy surfaces was constructed using the reproducing-kernel Hilbert space method [21] which has proved to be very effective for the description of several van der Waals systems including He-HF [22], He-F_2 [23], and H-F_2 [24], which we have also studied. One important aspect of this method is that the asymptotic behavior of the reproducing-kernel functions is known analytically and allows us to describe exactly the long-range part of the potential.

Cross sections were computed for kinetic energies in the range 10^{-6}–1000 in cm^{-1}. The ortho-N_2^+ and para-N_2^+ nuclear spin isomers were treated independently and convergence was checked as a function of the propagator step size. The maximum propagation distance was 2000 bohrs at the lowest collision energy. At each point of the propagation grid the matrix elements of the potential were computed by expanding the interaction potential in Legendre polynomials, retaining only even terms up to $\lambda = 12$ on a grid of ten points used to calculate the Gauss-Hermite quadrature of the vibrational part of the integral. The basis set included ten rotations per vibration and, respectively, one and two vibrational levels in the case of the rotational and vibrational quenching calculations for both the spin-free and spin-coupled calculations. In this basis set, the cross sections are converged to better than 1%. The maximum value of the total angular momentum J used in the spin-coupled calculations was $J = 101/2$.

III. RESULTS AND DISCUSSION

Our spin-rotation code was first checked by comparing a calculation in which the spin rotation constant γ was set to zero with the close-coupling $^1\Sigma$ results. The two types of results agreed exactly. We first considered the vibrational quenching of N_2^+ ($\nu = 1$, $N = 0$) in collisions with the two ^{3}He and ^{4}He isotopes, which was found to exhibit a very strong isotope effect in our previous spin-free study. The $N = 0$ state is the only one that yields only one parity state $j = 1/2$, $\varepsilon = -1$ when the spin coupling is included and therefore only one curve is associated with the spin-coupled results. The results of this previous study [12] [see Fig. 1(a) of this reference] were found to be in perfect agreement with those obtained from the present spin-coupled calculations. The resonance pattern is unchanged for both isotopes and the isotope effect is conserved. These results are in agreement with those of Balakrishnan *et al.* [11] who found that the vibrational quenching of CaH was not modified when the spin rotation is included.

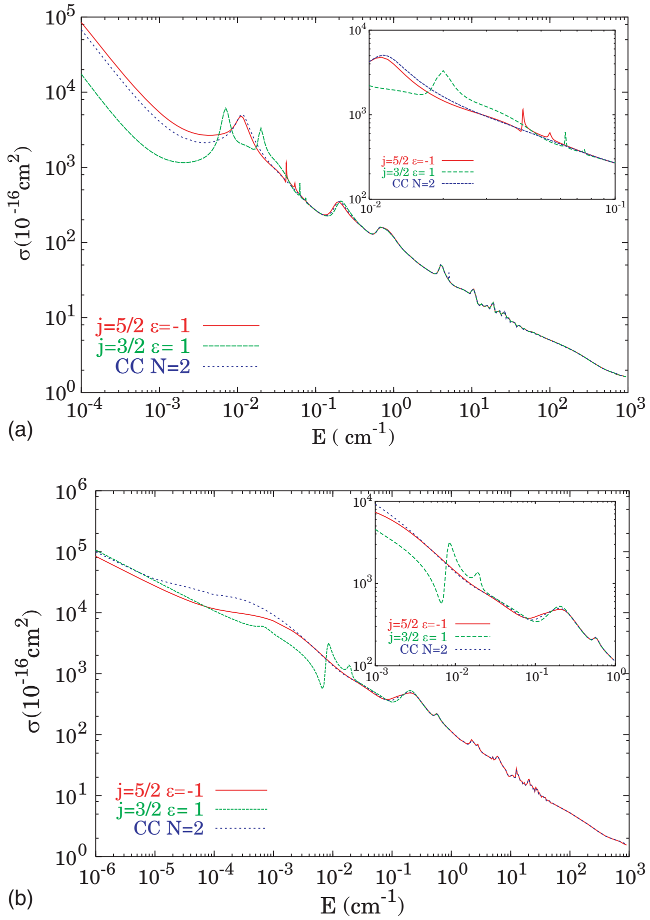

FIG. 1. (Color online) Comparison of the spin-free and spin-coupled results for the rotational quenching of $N_2^+(\nu=0, N=2)$ in collisions with (a) ^{3}He and (b) ^{4}He as a function of energy. The spin-free results are named CC $N=2$.

We then considered the spin-free results for the rotational quenching of N_2^+ ($\nu = 0$, $N = 2$) in collisions with the two He isotopes and found the same isotope effect that we obtained for the vibrational quenching. This result motivated the present study, as the recent work of Balakrishnan *et al.* [11] on CaH showed that, in contrast to vibrational quenching, rotational quenching is affected by the spin-rotation coupling. This is indeed what can be seen in Figs. 1(a) and 1(b) where the spin-coupled and spin-free calculations, respectively, are compared for the ^{3}He and ^{4}He isotopes. We notice first that both sets of results agree perfectly for energies above 1 cm^{-1}, and we will fix the highest energy at this value in the next figures. Figure 1(a) shows the suppression of the positive-parity rotational relaxation at very low energy. This can be understood by first noticing that the parity of the $N=0$ level is negative and that parity-conserving transitions are favored. This tendency was analyzed in the early studies of Lengel and Crosley [25] and Alexander and Corey [26] and shown to be due to the propensity toward conservation of orientation of rotational angular momentum. This is in contrast with the results of Balakrishnan *et al.* [11] who observed in the limit of zero collision energy the suppression of rotational relaxation of the negative-parity state of CaH ($N=1$, $j=3/2$, $\varepsilon=-1$). They attributed their result to the formation of Feshbach-type resonances due to trapping behind centrifugal barriers in the outgoing channels. Their results appear to be specific to the system that they studied.

If we now examine the resonance pattern for the ^{3}He-N$_2^+$ collision in Fig. 1(a) we see that, while the negative-parity curve reproduces perfectly the first spin-free resonance, the curve associated with the positive-parity state exhibits two low-energy resonances instead of one. The energy position of the first of these resonances corresponds to the doublet shifting of the $N=2$ level and is due to a Feshbach resonance associated with the opening of the negative-parity level of the $N=2$ doublet. This hypothesis is confirmed by the absence of resonance at this energy on the negative-parity curve. The second resonance is simply the spin-free shape resonance, which is shifted as a consequence of the presence of the new resonance. This analysis will be confirmed by looking at the total J partial analysis of this transition below.

Two other resonances can also be noticed at higher energies, this time on both curves associated with the two parities. They are shifted to higher energy by the energy doublet splitting on the negative-parity curve. This shift shows that they are not shape resonances but Feshbach resonances.

If we now turn to the curves associated with the ^{4}He isotope, which are shown in Fig. 1(b), we notice first that the suppression effect of the positive-parity rotational relaxation is not as large as it is for the ^{3}He isotope. This is possibly due to the presence of a broad resonance at very low energy, which was already present on the spin-free curve and is specific to this isotope. The positive-parity curve again exhibits a Feshbach resonance at the energy corresponding to the opening of the negative-parity level of the $N=2$ doublet, and again this resonance is missing on the curve associated with the negative-parity state. There is another resonance at a slightly higher energy not observed on the ^{3}He curve. It will be analyzed in the forthcoming partial wave analysis. Due to the change of the reduced mass, the two resonances at higher energy disappear from the curve in Fig. 1(b).

In Figs. 2(a) and 2(b), we present all the open deactivation transitions starting from the positive- and negative-parity states of the N$_2^+$ ($\nu=0$, $N=2$) level in ^{3}He+N$_2^+$ collisions. For the whole range of energy considered in this figure, the elastic cross sections are the largest. They are larger than the cross sections for rotational quenching, which are themselves larger than the fine-structure relaxation cross sections. Again we notice that the first Feshbach resonance can be found only for transitions out of the positive-parity state. The second of the higher-energy Feshbach resonances appears only on the curve associated with the ($N=0$, $\varepsilon=-1$) final state.

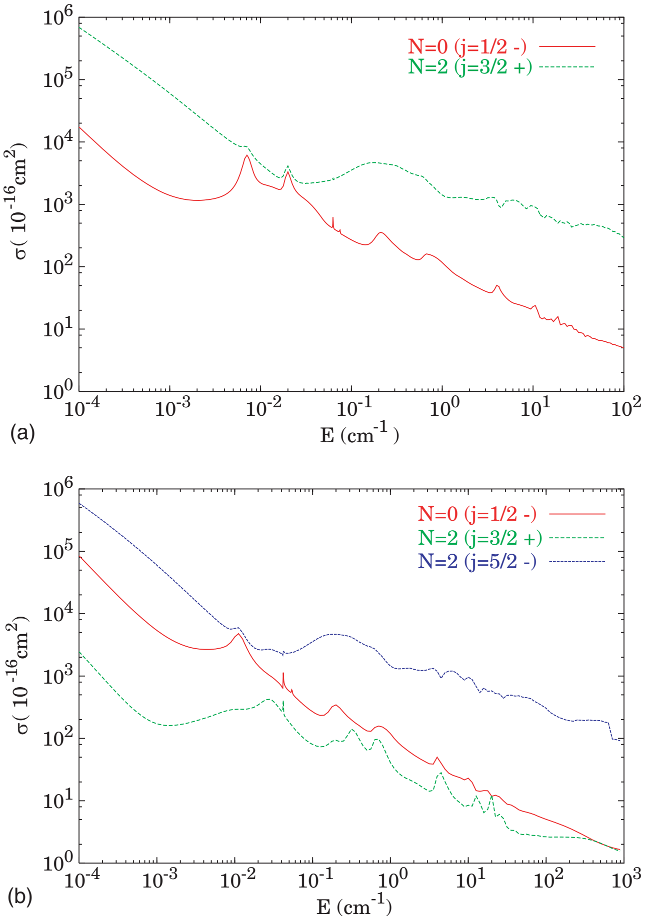

FIG. 2. (Color online) Comparison of the elastic and relaxation cross sections of (a) N$_2^+$($\nu=0,N=2,j=3/2,\varepsilon=+$) and (b) N$_2^+$($\nu=0,N=2,j=5/2,\varepsilon=-$) in collisions with ^{3}He as a function of energy.

The same representation was done for the ^{4}He+N$_2^+$ collision in Figs. 3(a) and 3(b). For energies below 10^{-3} cm^{-1}, this change of mass makes the elastic cross section smaller than that associated with the fine-structure transitions and that associated with rotational relaxation becomes the largest. One can also notice that a broad resonance appears in spin-free calculations at very low energy for transitions out of the positive-parity state. This can be understood by noticing that, when ^{3}He is replaced by ^{4}He, the reduced mass of the collision partners is multiplied by a factor of 1.3 and increases inelastic collisions. The effect of spin rotation on the inelastic energy transfer is then more difficult to see than for the collisions involving ^{3}He.

In order to further analyze the nature of the resonances, we performed a total J partial analysis of the ($N=2,\varepsilon=+$) $\rightarrow$($N=0,\varepsilon=-$) transition which is represented for the collisions involving ^{3}He and ^{4}He, respectively, in Figs. 4(a) and 4(b). Because we start from a nonzero value of j, the attribution of a single partial wave is possible only for the s wave in the initial ($J=j$) and final ($J=j'$) channels. Figure 4(a) shows that, for the ^{3}He isotope, the first two resonances starting from the positive-parity state are associated with the

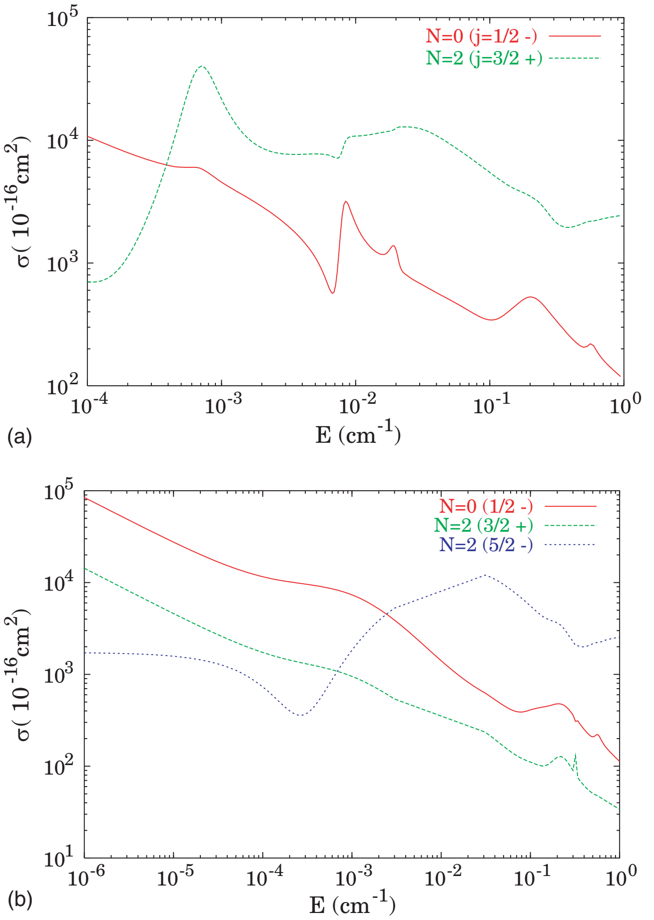

FIG. 3. (Color online) Comparison of the elastic and relaxation cross sections of (a) $N_2^+(\nu=0,N=2,j=3/2,\varepsilon=+)$ and (b) $N_2^+(\nu=0,N=2,j=5/2,\varepsilon=-)$ in collisions with ^{4}He as a function of energy.

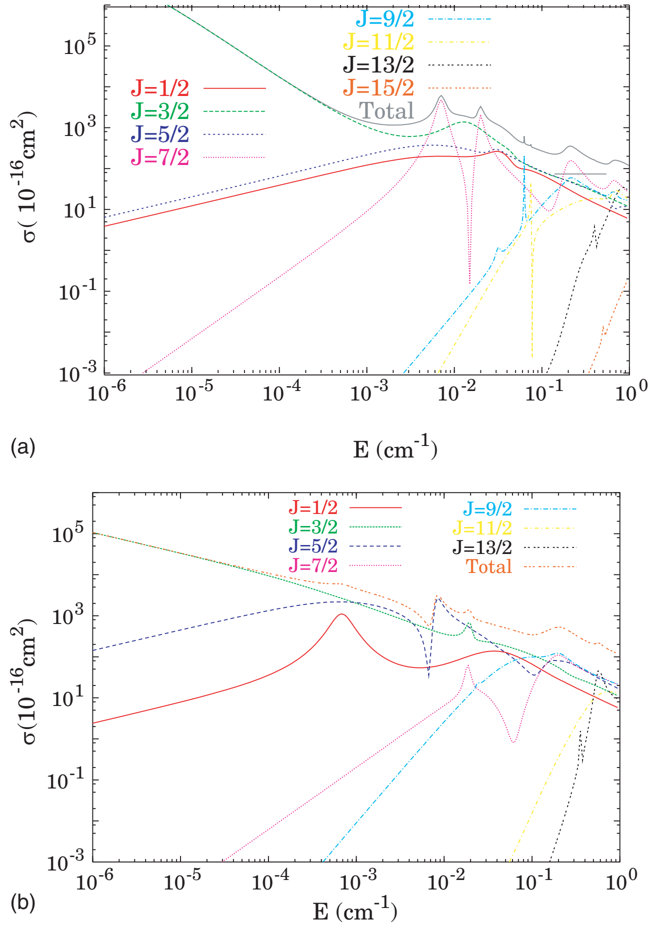

FIG. 4. (Color online) Total J partial analysis of the rotational quenching of (a) $N_2^+(\nu=0,N=2,j=3/2,\varepsilon=+)=>N_2^+(N=0,j=1/2,\varepsilon=-)$ in collisions with ^{3}He as a function of energy and (b) $N_2^+(\nu=0,N=2,j=3/2,\varepsilon=+)=>N_2^+(N=0,j=1/2,\varepsilon=-)$ in collisions with ^{4}He as a function of energy.

same value of $J=7/2$. Their interaction results in shifting the spin-free resonance to higher energy. This is in contrast with the situation for ^{4}He in Fig. 4(b). The first and second Feshbach resonances are associated with different values of $J=5/2$ and 3/2. The second resonance is clearly associated with $l=0$ and is due to the trapping behind the centrifugal barrier in the outgoing channel. Such kinds of resonance were identified by Balakrishnan *et al.* [11] for CaH. If we look carefully at the figure dedicated to ^{3}He, we see that a similar resonance is also present.

We have checked that these results are not limited to the $N=2$ level by performing similar calculations for higher values of N shown in Figs. 5(a) and 5(b). Here, we also see Feshbach resonances at the energy corresponding to the opening of the negative-parity level on the curve associated with the positive-parity state. This effect is, however, less pronounced than for $N=2$, as in higher rotational levels the efficiency of rotational energy transfer is much larger than that of fine-structure transitions for collision energies corresponding to the ultracold s-wave limit, as noticed already by Balakrishnan *et al.* [11] for CaH.

To extract general rules from this analysis that could be applied to other diatomic molecules with a different B/γ ratio, we increased the real value of $\gamma=8.3\times10^{-3}$ cm^{-1} to 1.3×10^{-2} cm^{-3} and decreased the ratio B/γ from 240 to 150. The resulting changes in the rotational quenching of the $N=2$ state are represented for both parities for the collisions involving ^{3}He and ^{4}He, respectively, in Figs. 6(a) and 6(b). The resonances are clearly shifted to either higher or lower energies depending on the parity of the initial level. This can be explained by Eq. (1). We see that, if γ is increased, the $\varepsilon=+$ parity levels are lowered and consequently the positions of the resonance are higher in energy and their amplitudes tend to be lowered. Conversely, and for the same reasons, the energies of the $\varepsilon=-$ parity levels increase and consequently the positions of the resonance are lower in energy and their amplitudes tend to be increased.

IV. CONCLUSION

In this study the effect of the spin-rotation interaction on the inelastic collision of a structureless atom (^{3}He and ^{4}He) with a charged $^2\Sigma^+$ molecule (N_2^+) was considered. The spin-rotation interaction is found not to affect vibrational quenching or elastic transitions, in agreement with previous

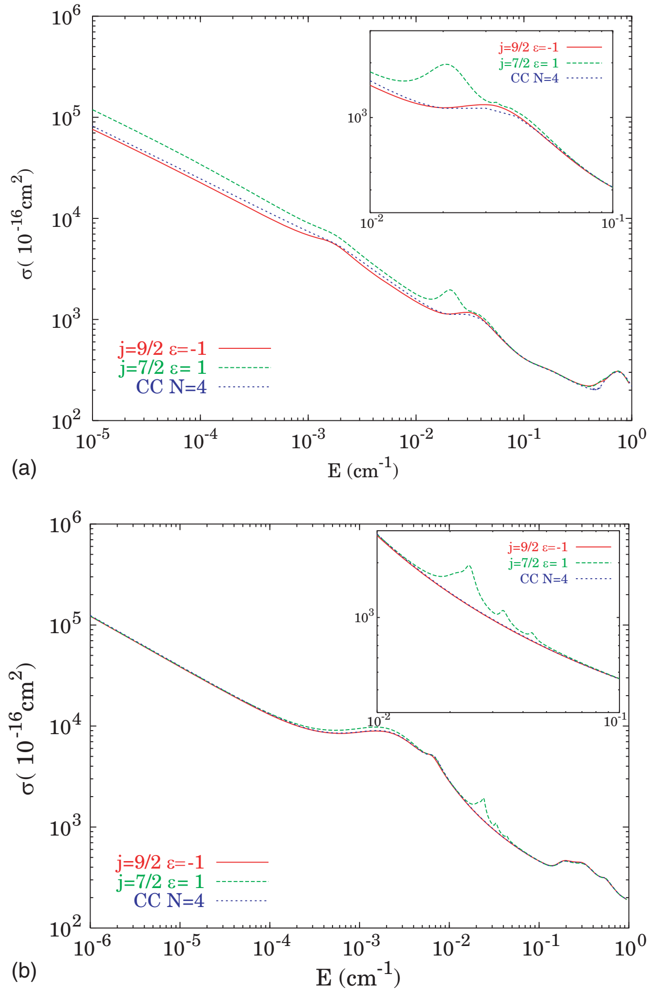

FIG. 5. (Color online) Comparison of the spin-free and spin-coupled results for the rotational quenching of $N_2^+(\nu=0,N=4)$ in collisions with (a) ^{3}He and (b) ^{4}He as a function of energy. The spin-free results are named CC $N=4$.

theoretical studies. Consequently, the isotope effect that we obtained for this process in our previous study devoted to He-N_2^+ is preserved. Conversely, the rotational quenching was found to be altered in the very low energy region, where the partial suppression of the positive-parity rotational relaxation was observed. This phenomenon appears to be a simple consequence of the fact that parity-conserving transitions are favored. This in turn is a consequence of the propensity for conservation of orientation of rotational angular momentum. This is in contrast with the results of Balakrishnan *et al.* [11], who observed in the limit of zero collision energy the suppression of rotational relaxation of the negative-parity state of CaH ($N=1$, $j=3/2$, $\varepsilon=-1$) in collisions with ^{3}He. We also found that a new Feshbach resonance appears within a doublet on the curve associated with the lowest-parity state at the energy of the splitting. Other Feshbach resonances appear at higher energies for both parities, which are more difficult to predict because they are more system dependent. Some of them were shown to be due to trapping behind the centrifugal barrier in the outgoing channel. To extract general rules from this analysis that could be applied to other diatomic molecules with a different B/γ ratio, we increased the positive value of the spin-rotation constant γ, which decreased the value of the $|B/\gamma|$ ratio. We found that the positions of the Feshbach resonances due to the spin-rotation coupling are higher in energy on the curves associated with the lowest parity level (here positive), and that their amplitudes tend to be lowered. Conversely, the positions of these resonances are lower in energy on the curves associated with the highest parity level (here negative), and their amplitudes tend to increase.

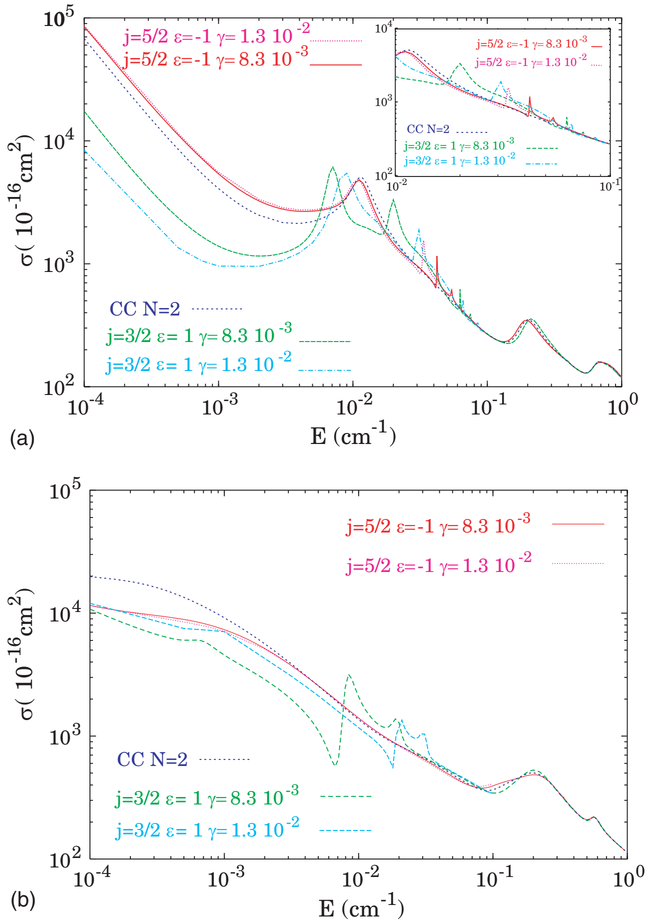

FIG. 6. (Color online) Comparison of the rotational quenching of $N_2^+(\nu=0,N=2,j=3/2,\varepsilon=+)$ and $N_2^+(\nu=0,N=2,j=5/2,\varepsilon=-)$ in collisions with (a) ^{3}He and (b) ^{4}He as a function of energy for two different values of the spin-rotation constant γ. The spin free results are also represented and named CC $N=2$.

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