

Fine-structure effects in vibrational relaxation at ultralow temperatures

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We have calculated cross sections for vibrational quenching in collisions of $^{17}\text{O}_2(X^3\Sigma_g^-)$ with ^3He at cold and ultracold temperatures, explicitly accounting for the electronic spin degree of freedom. The observed population of the final spin-rotational levels can be interpreted on the basis of useful “propensity rules” governing the intensity of the collision-induced transitions. In addition, it is found that the orientation of the molecular spin is reasonably robust against collisional relaxation, even in vibrationally excited states. This finding implies that magnetic trapping of vibrationally excited, but rotationally and translationally cold, molecules may be possible. © 2003 American Institute of Physics. [DOI: 10.1063/1.1577113]

I. INTRODUCTION

The possibility of creating cold and ultracold molecules has opened novel and interesting perspectives in the field of Bose–Einstein condensation, high resolution spectroscopy, and selective control of chemical reactions. In this spirit, substantial progress has been achieved in developing and optimizing experimental techniques for trapping and cooling molecules at sub-Kelvin temperatures. Cold molecules are produced primarily via one of three experimental techniques: (i) collisions with a helium buffer gas;^{1–3} (ii) assembling cold atoms via photoassociation^{4–8} or magnetic field sweeps;⁹ or (iii) electrostatic slowing if the molecules have a permanent electric dipole moment.^{10–12}

Collisions can play a decisive role in these experiments. For example, in buffer-gas cooling, elastic collisions between molecules and buffer gas atoms thermalize the sample at temperature of the order of a fraction of a Kelvin. The critical requirement for the success of this technique is that thermalizing elastic collisions should be much more efficient than the inelastic transitions that can lead to antitrapped states and subsequent trap loss.¹³ In photoassociation, the resulting molecules are translationally very cold (in the order of μK 's), but they are produced preferentially in high-lying vibrational levels of the ground electronic states. Vibrational relaxation is then a central issue, because it involves energies which are orders of magnitude larger than the depth of the trap. In this context, vibrational de-excitation can be quite efficient, seriously limiting the density of molecules in the trap.¹⁴

For these reasons, vibrational quenching has drawn considerable theoretical attention.^{15–22} In particular, Ref. 19 found that the distribution of rotational final states is narrower in ultralow temperature collisions than at higher temperatures. It also found that vibrational quenching can be far less efficient than rotational quenching, leading to the possibility of vibrationally excited, but translationally and rota-

tionally cold, molecular gases. Here we extend the results of Ref. 19 by explicitly including the fine structure. In this way we will verify that vibrationally excited states are stable against changes in spin orientation, so that magnetic trapping experiments of these states are possible. Along the way, we will investigate fine-structure-changing processes in vibrational quenching collisions, which are roughly explained by simple propensity rules.

II. THEORY

We will concentrate on collisions between helium atoms and oxygen molecules in their electronic $^3\Sigma_g^-$ ground states, which we have investigated in the past.^{23–26} In this work, we investigate vibrational relaxation in collisions of $^{17}\text{O}_2$ with ^3He . The choice of $^{17}\text{O}_2$ is due to the better cooling perspectives offered by this isotopomer.^{23,24} Vibrational de-excitation for this system has been already studied by Balakrishnan and Dalgarno, who performed calculations for the isotopomer $^{16}\text{O}_2$ but without including the electronic spin.¹⁹

The theory and the formalism of the scattering equations have been given in Ref. 27, and will be briefly recalled here.

We will consider molecules consisting of two ^{17}O atoms, whose nuclear spin i is equal to 5/2. We assume that total nuclear spin $\mathbf{I} = \mathbf{i}_1 + \mathbf{i}_2$ is conserved in the collision, implying that the even molecular rotational states N belong to a manifold separated from the odd ones.²⁸ Following Refs. 24–26, we limit our discussions to the “even- N ” manifold of molecular states.

The molecules have total spin $\mathbf{J} = \mathbf{N} + \mathbf{S}$, where S is the electronic spin and equals 1 for O_2 . The Hamiltonian operator $\hat{\mathbf{H}}_{\text{O}_2}$ for molecular oxygen is given as

$$\hat{\mathbf{H}}_{\text{O}_2} = -\frac{\hbar^2}{2\mu_{\text{O}_2}} \left[\frac{d^2}{dr^2} - \frac{N(N+1)}{r^2} \right] + V(r) + \hat{\mathbf{H}}_{\text{fs}}, \quad (1)$$

where μ_{O_2} is the O–O reduced mass and V is the atom–atom potential depending on the stretching coordinate r . We have taken the fine-structure Hamiltonian $\hat{\mathbf{H}}_{\text{fs}}$ from Ref. 29 disre-

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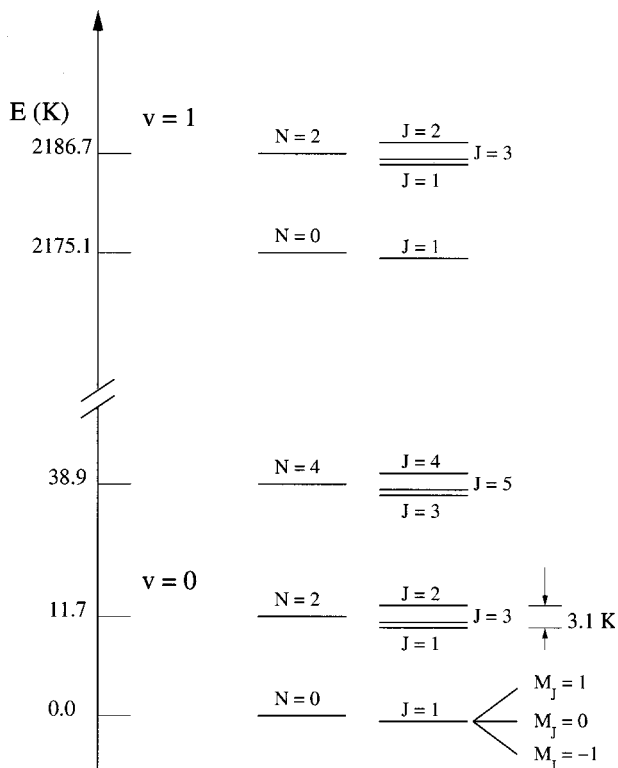


FIG. 1. The spin-rotational structure of the oxygen molecule. The $v = 1$ manifold is also shown to emphasize the different energy scales for spin, rotational, and vibrational separations. In zero external magnetic field, different value of M_J belonging to the same $|N, J\rangle$ pair are degenerate.

garding the molecular hyperfine interaction and using the fine structure parameters determined in Ref. 30 by microwave spectroscopy. We assume these parameters to be the same for the ground and excited vibrational states.

Different values of the molecular rotational quantum number N are coupled together by the fine-structure Hamiltonian \hat{H}_{fs} [see Eq. (A5) in Ref. 29], so that N is no longer strictly a good quantum number for the molecular states. However, since the fine-structure coupling is small compared to the rotational separation, different N 's are mixed only weakly, so we will continue to use N to label the true channels in what follows.

A schematic representation of the $^{17}\text{O}_2$ rovibrational structure is sketched in Fig. 1. The zero-point energy is ~ 1100 K above the bottom of the potential curve, and the vibrational separation between the ground and the first excited vibrational level is ~ 2175 K. The rotational constant for the molecule is about 1.95 K, and the spin-orbit coupling is a small perturbation on the rotational levels.

After multiplying the wave function by R in order to remove first derivatives, the full Hamiltonian operator describing the He- O_2 collision is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left[\frac{d^2}{dR^2} - \frac{\hat{L}^2}{R^2} \right] + \hat{H}_{\text{O}_2} + V'(R, r, \theta), \quad (2)$$

where μ is the reduced mass for the He- O_2 system, R is the length of the Jacobi vector joining the atom to the molecule center-of-mass, \hat{L}^2 is the centrifugal angular momentum op-

erator, and \hat{H}_{O_2} is the molecular oxygen Hamiltonian defined in Eq. (1). The potential term V' , depending in general on R , r , and the bending angle θ that the molecule's axis makes with respect to \mathbf{R} , accounts for the He- O_2 interaction. The O-O interatomic contribution is already included in the molecular Hamiltonian \hat{H}_{O_2} .

The full multichannel calculation requires casting $V'(R, r, \theta)$ in an appropriate angular momentum basis. Namely, we express the Hamiltonian in a basis of total angular momentum $\mathcal{J} = \mathbf{N} + \mathbf{S} + \mathbf{L}$, in terms of the molecule's mechanical rotation (\mathbf{N}), its electronic spin (\mathbf{S}), and the partial wave representing the rotation of the molecule and the He atom about their center of mass (\mathbf{L}). Our basis for close-coupling calculations is then

$$[\text{O}_2(^3\Sigma_g^-)]|\text{He}(^1S)\rangle|vN[JM]\mathcal{J}\mathcal{M}\rangle, \quad (3)$$

where the electronic spin quantum number S is not explicitly indicated, being always equal to 1 in the calculation presented here. Vibrational wave functions are computed for a particular value of N then transformed to the J basis. Evaluation of V' in the basis (3) has been discussed in Ref. 24. As for the integration of the matrix elements over the vibrational coordinate r , we have performed numerical Gaussian quadratures.

Once the Hamiltonian is in place the coupled-channel equations are solved subject to scattering boundary conditions to yield scattering matrices. Since we assume zero magnetic field the total angular momentum \mathcal{J} is a good quantum number, and moreover the results are independent of the laboratory projection \mathcal{M} of total angular momentum. In the context of magnetic trapping, the resulting total- \mathcal{J} scattering matrices can be conveniently transformed to a basis labeling the magnetic quantum numbers, namely $\langle vNJM_JLM_L|S|v'N'J'M'_JL'M'_L\rangle$. Cross sections and state-to-state rate coefficients are then obtained as in Ref. 24

$$\sigma_{vNJM_J \rightarrow v'N'J'M'_J} = \frac{\pi}{k_{vNJM_J}^2} \sum_{LM_L L'M'_L} |\langle vNJM_JLM_L|S - I|v'N'J'M'_JL'M'_L\rangle|^2 \quad (4)$$

and

$$K_{vNJM_J \rightarrow v'N'J'M'_J} = v_{vNJM_J} \sigma_{vNJM_J \rightarrow v'N'J'M'_J}, \quad (5)$$

where v_{vNJM_J} is the relative velocity of the collision partners before the collision.

In this work, we use the *ab initio* potential energy surface (PES) by Groenenboom and Struniewicz,³¹ which accounts for the vibrational degree of freedom of the O_2 molecule. This PES differs from the one by Cybulski *et al.*³² used in a previous calculation by one of the authors.²⁴ In particular, the potential well for the three-body interaction is found to be about 30% deeper for the new PES with respect to the preceding one [however, the PES (Ref. 32) was deepened by 20% in the calculations presented in Ref. 24]. The two potential surfaces provide consistent results: the *s*-wave scattering lengths are ~ -2.9 a.u. and ~ -1.5 a.u. using the PES of Refs. 31 and 32, respectively.

III. PROPENSITY RULES

In the 1980s, Alexander *et al.* published some very useful papers about the description of inelastic collisions involving open-shell diatomic molecules.^{33,34} In this work, a framework is provided in order to describe the coupling between the relative motion of the collisional encounters and the spin-rotational angular momentum of the molecule. In Ref. 34, the authors investigated rotational transitions for the same system we are concerned with, obtaining some tools to simplify the scattering problem and propensity rules for the interpretation of the observed transitions. In what follows, we will briefly outline the main findings of that work, as they are relevant to the subject investigated here.

The basic idea was that, since the atom-molecule intermolecular potential does not contain any magnetic terms, in the collision dynamics the electronic spin \mathbf{S} plays a spectator role. This mechanism can be exploited to rigorously decouple the electronic spin angular momentum from the rotational-centrifugal motion.³⁵⁻³⁸ In a pure Hund's case (b) molecule, Corey and McCourt derived a recoupling algorithm to express the crucial elements $T_{NSJL \rightarrow N'S'J'L'}^{\mathcal{J}}$ of the T matrix governing the collision-induced fine-structure transitions in terms of the spin-independent elements $T_{NL \rightarrow N'L'}^{\mathcal{J}}$. Alexander *et al.* extended the vector recoupling algorithm to the case of weak mixing of the pure case (b) states in a Σ -state molecule,³⁴ as we have here. For the picture of electronic spin in a spectator role to hold, no magnetic field can be applied.

Propensity rules governing the intensity of the transitions have been derived in that context, and will be recalled here since they are very relevant in the interpretation of our own dynamical results. Since they have been derived using only the angular momentum algebra needed to describe the molecular states, these rules maintain their validity regardless of the specific vibrational level they are applied to.

In Hund's case (b), fine structure levels correspond to different orientations of \mathbf{N} with respect to \mathbf{S} . In spectroscopic notation, for Σ electronic states the levels are labeled by the index F_i . In the case of O_2 , S equals 1 and we have

$$F_1: J=N+1; \quad F_2: J=N; \quad F_3: J=N-1. \quad (6)$$

References 39 and 40 show that collision-induced transitions which conserve F_i are strongly favored. Since the atom-molecule interaction does not contain magnetic terms, a collision does not change the orientation of \mathbf{S} and the propensity toward the conservation of F_i can be interpreted as the collisional propensity toward the conservation of the orientation of \mathbf{N} . This argument can be made more quantitative by introducing an angular momentum transfer index K , which can be interpreted classically as the degree of reorientation of the nuclear rotational angular momentum,

$$K = |N - N'| = |L - L'|. \quad (7)$$

The T-operator (and the cross sections that follow from it) can be expressed as a sum of irreducible tensorial components of order K . The contribution of each term decreases as K increases, which is in fact a manifestation of the propensity toward the conservation of the orientation of \mathbf{N} . This

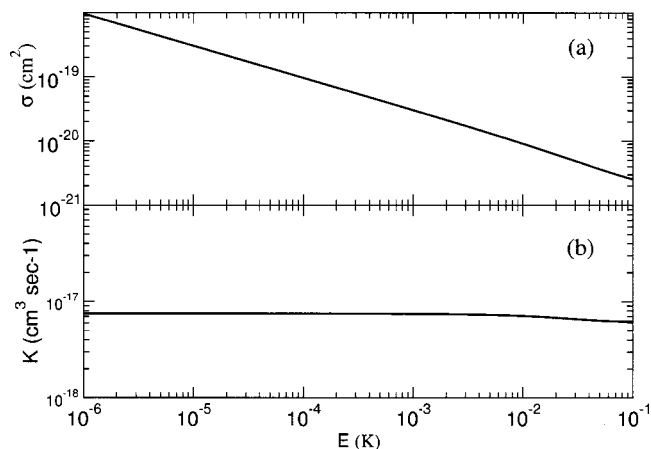


FIG. 2. Cross sections [panel (a)] and rate coefficients [panel (b)] for the overall vibrational quenching (that is summed over all the final states of the $v=0$ manifold) of the $|v N J\rangle = |1 0 1\rangle$ incident state, in the range of collision energy from 10^{-6} to 10^{-1} K.

implies that largest cross sections are expected to be the ones corresponding to $\Delta N = \Delta J$, and that this propensity will become increasingly stronger as N (or N') increases. If a molecule is initially in a certain F_i state, the tendency is to populate after the collision a final state with $F'_i = F_i$. From analogous arguments, it is also possible to derive a rule that forbids transitions $F_2 \leftrightarrow F_1, F_3$ if $M_J = M'_J = 0$.

IV. VIBRATIONAL QUENCHING

In the present paper, vibrational quenching has been restricted to the $v=1$ rotational manifolds of the oxygen molecule. We have retained in the calculations rotational levels up to $N=24$ both for the ground and the excited vibrational state, plus 24 partial waves. We have studied a large number of collision energies ranging from 1 μ K up to 10 K. The maximum value of the total angular momentum \mathcal{J} to be considered (and consequently the computational effort) is, of course, a function of the incident energy. In the most demanding case, total \mathcal{J} values up to 8 have been included.

Scattering calculations are performed using a log-derivative propagator method⁴¹ starting from $R=4.2$ Bohr. We separate the propagation into two parts, from $R=4.2$ to 24.0 Bohr, with a step size of 0.008 Bohr, and then from $R=24.0$ until the asymptotic limit of $R_{\max}=450$ Bohr adopting a larger step size of 0.08 Bohr. These parameters assure rate constants convergent within less than 1%.

In this section, we will discuss our results on the vibrational quenching transition $v=1 \rightarrow v=0$. In the next section, we will consider explicitly the efficiency of the spin-rotational de-excitation within the $v=1$ manifold itself.

We consider first the initial state $|v N J\rangle = |1 0 1\rangle$ (the three magnetic projections $M_J=0, \pm 1$ are degenerate in zero external field), and examine the efficiency to populate the $v=0$ spin-rotational manifold. In Fig. 2 we have plotted cross sections [panel (a)] and rate coefficients [panel (b)] for the overall vibrational quenching, summed over the possible $|N J\rangle$ states belonging to $v=0$. Results refer to the range of collision energy 10^{-6} – 10^{-1} K. It is evident in the figure that below 10^{-2} K we are in the threshold regime and cross sec-

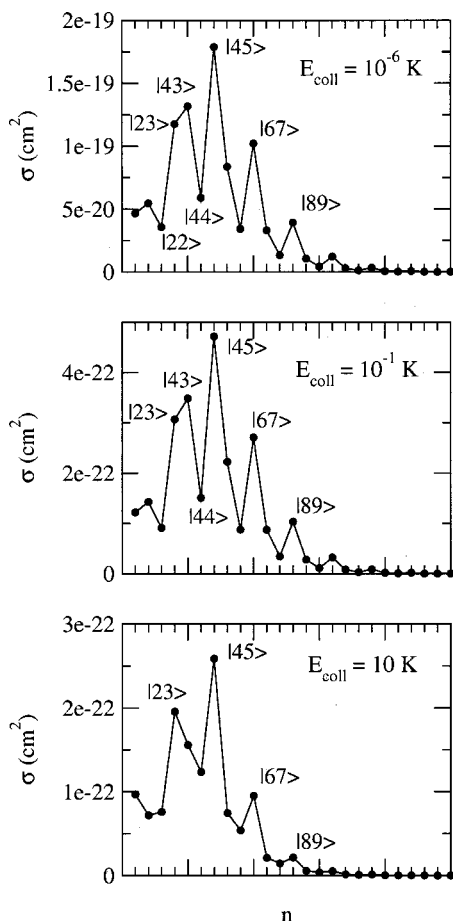


FIG. 3. State-resolved cross sections for the collisional quenching of the initial state $|v N J\rangle = |1 0 1\rangle$. Panels refer to the indicated collision energies: 10^{-6} , 10^{-1} , and 10 K. The x -axis label n is an index counting the final states according to the rule $n=1 \rightarrow |0 0 1\rangle$, $n=2 \rightarrow |0 2 1\rangle$, $n=3 \rightarrow |0 2 2\rangle$, $n=4 \rightarrow |0 2 3\rangle$, and so on. For clarity, in each panel some of the populated final states of $v'=0$ are indicated.

tions vary inversely as the velocity in accordance with Wigner's law. Rate coefficients become constant in this limit of very low collision energy, and approach a value close to the one obtained by Balakrishnan and Dalgarno for the isotopomer $^{16}\text{O}_2$: The zero-temperature limiting values of the vibrational quenching rate coefficients are equal to $5.22 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ and $7.51 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ in Ref. 19 and for the present case, respectively. The low value of the coefficients is due to the suppression of all partial waves other than $L=0$. In this range of energy, calculations can be restricted to total angular momentum $J=1$.

For higher collision energies, the overall picture is complicated by both Feshbach and shape resonances, whose existence has been proved in previous papers.¹⁹ These resonances are expected to produce a broad feature in the thermally-averaged collision rates (see Fig. 2 of Ref. 19), and should thus provide even more detailed insight into quenching collisions.

In Fig. 3 we show a detailed analysis of the final population for three selected collision energies, 10^{-6} , 10^{-1} , and 10 K. Again, we consider the initial state $|v N J\rangle = |1 0 1\rangle$. Some of the states significantly populated after the quenching are labeled. The incident channel is an F_1

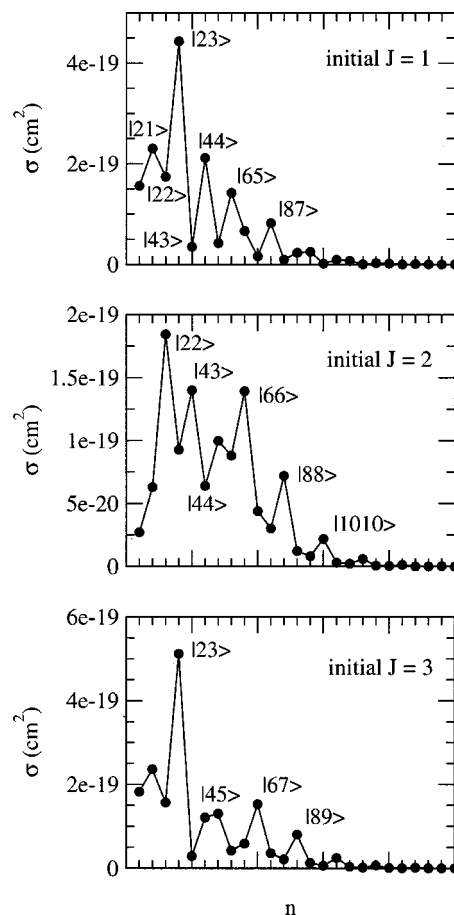


FIG. 4. Cross sections for the vibrational de-excitation of the initial state $|v N J\rangle = |1 2 1\rangle$ (first panel), $|1 2 2\rangle$ (second panel), and $|1 2 3\rangle$ (third panel). The collision energy is 10^{-6} K. As in Fig. 3, we have labeled for clarity some of the most populated final states.

state, that is $J=N+1$. For each $|v'=0, N'\rangle$ multiplet, corresponding to the spin splitting of the rotational levels, the final state F'_1 is always the most likely to be populated by the collision-induced transition. This is in accordance with the propensity rule $\Delta N = \Delta J$ derived by Alexander, and the same conclusion holds for the three investigated energies. This trend is verified as well for increasing final N' , but cannot be seen in the figure because of the low probability of transitions corresponding to large ΔN . While in general the propensity rules hold, it is also true that non- N -conserving collisions occur. The fact that incident collision energies are far smaller than fine structure intervals in the molecules raises possibilities for selecting individual initial states experimentally, and therefore to probe deviations from the simple expectation rules.

In order to verify how general are the conclusions drawn here, we have selected different initial states and repeated the same analysis. Let us consider the incident channels $|v N J\rangle = |1 2 1\rangle$, $|1 2 2\rangle$, and $|1 2 3\rangle$, at the collision energy of $1 \mu\text{K}$. Different energies have been investigated as well, leading to the same conclusions. In Fig. 4 we show the final distribution of the population for the vibrational quenching of the three possible initial states $J=1, 2$, and 3 (first, second, and third panel, respectively). It is evident the propensity towards the conservation of N , as mentioned in Sec. III.

TABLE I. Cross sections for the elastic, spin-rotational and vibrational relaxation transitions for the incident channels $|v N\rangle=|1 2\rangle$ and $|1 4\rangle$, for all possible J values. Initial (unprimed) and final (primed) states and collision energies are indicated. For transitions leading to $v'=0$, we only report the final states having the highest probability to be populated. The collision energy is 10^{-6} K.

$ v N J\rangle$	$ v' N' J'\rangle$	σ (cm ²)
$E_{\text{coll}}=10^{-6}$ K		
$ 1 2 1\rangle$	$ 1 0 1\rangle$	1.92×10^{-12}
$ 1 2 1\rangle$	$ 1 2 1\rangle$	2.47×10^{-15}
$ 1 2 1\rangle$	$ 0 2 3\rangle$	4.44×10^{-19}
$ 1 2 2\rangle$	$ 1 0 1\rangle$	3.47×10^{-13}
$ 1 2 2\rangle$	$ 1 2 1\rangle$	3.16×10^{-13}
$ 1 2 2\rangle$	$ 1 2 2\rangle$	1.48×10^{-15}
$ 1 2 2\rangle$	$ 1 2 3\rangle$	1.80×10^{-13}
$ 1 2 2\rangle$	$ 0 2 2\rangle$	1.84×10^{-19}
$ 1 2 3\rangle$	$ 1 0 1\rangle$	2.13×10^{-12}
$ 1 2 3\rangle$	$ 1 2 1\rangle$	4.60×10^{-16}
$ 1 2 3\rangle$	$ 1 2 3\rangle$	3.32×10^{-15}
$ 1 2 3\rangle$	$ 0 2 3\rangle$	5.12×10^{-19}
$ 1 4 3\rangle$	$ 1 0 1\rangle$	2.81×10^{-13}
$ 1 4 3\rangle$	$ 1 2 1\rangle$	9.77×10^{-13}
$ 1 4 3\rangle$	$ 1 2 2\rangle$	4.08×10^{-13}
$ 1 4 3\rangle$	$ 1 2 3\rangle$	1.38×10^{-13}
$ 1 4 3\rangle$	$ 1 4 3\rangle$	1.18×10^{-15}
$ 1 4 3\rangle$	$ 0 4 3\rangle$	1.98×10^{-19}
$ 1 4 4\rangle$	$ 1 0 1\rangle$	7.91×10^{-14}
$ 1 4 4\rangle$	$ 1 2 1\rangle$	2.19×10^{-13}
$ 1 4 4\rangle$	$ 1 2 2\rangle$	1.17×10^{-12}
$ 1 4 4\rangle$	$ 1 2 3\rangle$	1.52×10^{-13}
$ 1 4 4\rangle$	$ 1 4 3\rangle$	4.38×10^{-14}
$ 1 4 4\rangle$	$ 1 4 4\rangle$	9.87×10^{-16}
$ 1 4 4\rangle$	$ 1 4 5\rangle$	6.41×10^{-14}
$ 1 4 4\rangle$	$ 0 4 4\rangle$	2.03×10^{-19}
$ 1 4 5\rangle$	$ 1 0 1\rangle$	2.99×10^{-13}
$ 1 4 5\rangle$	$ 1 2 1\rangle$	2.83×10^{-14}
$ 1 4 5\rangle$	$ 1 2 2\rangle$	4.55×10^{-14}
$ 1 4 5\rangle$	$ 1 2 3\rangle$	1.44×10^{-12}
$ 1 4 5\rangle$	$ 1 4 3\rangle$	2.52×10^{-19}
$ 1 4 5\rangle$	$ 1 4 5\rangle$	1.38×10^{-15}
$ 1 4 5\rangle$	$ 0 4 5\rangle$	2.77×10^{-19}

In the case of the channel $|v N J\rangle=|1 2 3\rangle$, the propensity rule $\Delta N=\Delta J$ applies to all the transitions, while in the case of the channel $|v N J\rangle=|1 2 2\rangle$ the rule holds for all the final N' but $N'=4$. Finally, for $|v N J\rangle=|1 2 1\rangle$, the propensity rule starts to be valid for $N'>4$, and is increasingly respected (as it was expected to be) as N' increases.

V. PERSPECTIVES FOR TRAPPING EXPERIMENTS

So far, we have paid attention to the vibrational relaxation process. But how efficient is the rotational quenching within the $v=1$ manifold? In order to answer this question, we have selected as initial states the six states corresponding to the multiples $|v N\rangle=|1 2\rangle$ and $|1 4\rangle$ with all possible J values, and we have calculated cross sections for the elastic scattering and for spin-rotational transitions. These must then be compared with the corresponding cross sections for the vibrational relaxation. Results are shown in Table I and II for two sample collision energies. As for the vibrational relaxation, we report cross sections for the final state having the highest probability to be populated. Thermalizing elastic collisions have cross sections of the order of 10^{-15} cm², while

TABLE II. As in Table I, but for collision energy equal to 0.1 K.

$ v N J\rangle$	$ v' N' J'\rangle$	σ (cm ²)
$E_{\text{coll}}=0.1$ K		
$ 1 2 1\rangle$	$ 1 0 1\rangle$	6.13×10^{-15}
$ 1 2 1\rangle$	$ 1 2 1\rangle$	1.33×10^{-15}
$ 1 2 1\rangle$	$ 0 2 3\rangle$	1.40×10^{-21}
$ 1 4 4\rangle$	$ 1 0 1\rangle$	2.56×10^{-16}
$ 1 4 4\rangle$	$ 1 2 1\rangle$	5.23×10^{-16}
$ 1 4 4\rangle$	$ 1 2 2\rangle$	3.17×10^{-15}
$ 1 4 4\rangle$	$ 1 2 3\rangle$	5.06×10^{-16}
$ 1 4 4\rangle$	$ 1 4 3\rangle$	1.31×10^{-16}
$ 1 4 4\rangle$	$ 1 4 4\rangle$	2.02×10^{-15}
$ 1 4 4\rangle$	$ 1 4 5\rangle$	1.51×10^{-16}
$ 1 4 4\rangle$	$ 0 4 4\rangle$	5.43×10^{-22}

the most relevant process is the rotational relaxation, characterized by σ 's of the order of 10^{-12} – 10^{-13} cm² at collision energy as large as 1 μ K, and of the order of 10^{-15} cm² at collision energy equal to 0.1 K. Therefore, we can argue that a molecule trapped in an excited vibrational state will undergo an efficient rotational quenching, ending up in the ground rotational level $|v N J\rangle=|1 0 1\rangle$ of the excited vibrational state.

On the other side, molecules seem to be pretty stable with respect to vibrational de-excitation, since the vibrational motion is quenched much less efficiently: typical cross sections are of the order of 10^{-19} cm² at 1 μ K or smaller for higher energies (see also previous section). It is also worth to notice how the propensity rule holds very well in predicting the intensity of transitions to the $v=0$ manifold: largest cross sections are found for transitions that conserve N and for which $\Delta N=\Delta J$. As noted in Ref. 19, this allows for the possibility that vibrationally excited molecules could relax to rotationless states without necessarily quenching vibrationally.

A final ingredient for successful magnetic trapping of molecules is that the spin orientation, indexed by M_J , is also robust under collisions. This is because the molecules can only be trapped in their “weak-field-seeking” states whose Zeeman energy rises with increasing magnitude of the magnetic field.⁴² We have therefore investigated the collision processes of the ground spin-rotational state of $v=1$, $|v N J M_J\rangle=|1011\rangle\rightarrow|101M'_J\rangle$. Three values of the projection M_J are allowed for this state, namely, $M_J=1, 0$, and -1 . The trappable state (that is the one whose energy grows as the external magnetic field increases) is $|v N J M_J\rangle=|1 0 1 1\rangle$, which can give rise to either thermalizing elastic collisions or to spin-changing collisions that populate the antitrapped states $|1 0 1 0\rangle$ and $|1 0 1 -1\rangle$. These transitions are the ones responsible for trap loss.

Both elastic and inelastic cross sections are plotted in Fig. 5 as a function of the collision energy. The curve labeled “spin-changing” is the sum of the two transitions to $M_J=0$ and -1 . We have repeated the same calculation at collision energy equal to 10 K obtaining 2.86×10^{-14} cm² and 1.18×10^{-16} cm² for the elastic and spin-changing process, respectively. In the range of collision energies from 1 μ K to 0.1 K, which is relevant for buffer-gas cooling, cross sections for elastic collisions are significantly higher than the ones for

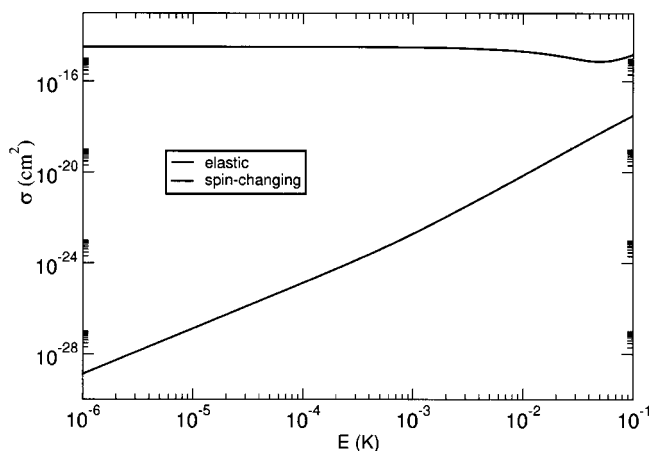


FIG. 5. Elastic and spin-changing cross sections for the incident channel $|v N J M_J\rangle = |1 0 1 1\rangle$ as a function of the collision energy. Spin-changing transitions lead to the population of the final states $|1 0 1 0\rangle$ and $|1 0 1 -1\rangle$, whose contributions have been summed.

spin-flipping transitions. These cross sections are very similar to those for the corresponding state of the ground vibrational manifold, $|v N J M_J\rangle = |0 0 1 1\rangle$, that have been discussed in Refs. 24 and 26. Hence the stability of the spin projection is not strongly influenced by the vibrational degree of freedom in this situation. In the zero field limit, the antitrapped states are energetically degenerate with the incident channel, but the spin-flipping requires boosting the centrifugal angular momentum L from 0 to 2, originating a centrifugal barrier in the exit channel whose height is about 0.59 K for the investigated system. As a result, spin-changing transitions are strongly suppressed by the Wigner's threshold laws as long as the collision energy does not exceed the height of the exit channel centrifugal barrier.

For higher collision energies inelastic transitions become quite effective, and cross sections become comparable with the elastic ones. In addition, the presence of both Feshbach and shape resonances, as proved in previous papers,²⁴ may further boost the spin-flipping transitions.

By analogy with the $v=0$ molecules studied in Ref. 26, we can assert that molecules in the state $|v N J M_J\rangle = |1 0 1 1\rangle$ are suitable candidates for magnetic trapping at low collision energies, although we have to keep in mind that results shown here refer to the zero field limit and inelastic rates are boosted by several orders of magnitude as soon as the field is turned on.²⁶

Concluding, we have characterized in this paper the collisional robustness of vibrationally excited oxygen molecules colliding with helium. We have verified that vibrational quenching remains fairly inefficient, even when the spin degree of freedom is included, as expected. Moreover, we have found that, for the lowest weak field seeking state of the excited vibrational manifold, elastic collisions dominate at low energies over inelastic, spin-changing transitions, exactly as in the case of ground vibrational level.²⁶ The same physical reasons are invoked to explain this result.

On the experimental side, results presented here may open some interesting perspectives for magnetically trapping

molecules in excited vibrational states. On the theoretical side, it would be interesting to investigate how present conclusions are affected by the presence of an external field, and to verify, as an ultimate goal, the possibility of influencing vibrational quenching via magnetically-tuned Feshbach resonances.

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