Quantum Dynamics of Ultracold Na + Na_2 Collisions

Pavel Soldán, Marko T. Cvitaš, and Jeremy M. Hutson
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

Pascal Honvault and Jean-Michel Launay
UMR 6627 du CNRS, Laboratoire de Physique des Atomes, Lasers, Molécules et Surfaces, Université de Rennes, France

(Received 3 May 2002; published 18 September 2002)

Ultracold collisions between spin-polarized Na atoms and vibrationally excited Na_2 molecules are investigated theoretically, using a reactive scattering formalism (including atom exchange). Calculations are carried out on both pairwise additive and nonadditive potential energy surfaces for the quartet electronic state. The Wigner threshold laws are followed for energies below 10^{-5} K. Vibrational relaxation processes dominate elastic processes for temperatures below 10^{-3}–10^{-4} K. For temperatures below 10^{-5} K, the rate coefficients for vibrational relaxation ($v = 1 \rightarrow 0$) are 4.8×10^{-11} and 5.2×10^{-10} cm^3 s^{-1} for the additive and nonadditive potentials, respectively. The large difference emphasizes the importance of using accurate potential energy surfaces for such calculations.

DOI: 10.1103/PhysRevLett.89.153201 PACS numbers: 34.50.–s, 03.75.Fi

Methods for creating diatomic molecules in atomic Bose-Einstein condensates (BECs) are now starting to be realized experimentally. They include photoassociation spectroscopy [1–4] and magnetic tuning through a Feshbach resonance [5,6]. An important long-range goal of such experiments is the production of a stable molecular BEC. However, in most cases the molecules are produced initially in vibrationally excited states, and their lifetime is limited by collisions with other atoms or molecules. Since the magnetic trap depth is typically 1 mK, any vibrationally or rotationally inelastic collision will release enough kinetic energy for both collision partners to be ejected from the trap.

Very little is known about vibrational relaxation rates for ultracold alkali dimers. Wynar *et al.* [2] produced $^{87}Rb_2$ molecules in very high vibrational levels of the ground electronic state in an atomic BEC by stimulated Raman scattering. They analyzed their line shapes to obtain an upper bound on the inelastic rate coefficient $k^{\mathrm{inel}} < 8 \times 10^{-11}$ cm^3/s. In subsequent experiments [7] on ultracold (but not condensed) Rb_2 molecules in a different set of vibrational levels, they measured $k^{\mathrm{inel}} = 3 \times 10^{-11}$ cm^3/s. These rates are too high for the production of long-lived molecules, but there is a hope that lower-lying states will relax more slowly [8,9] and that methods for stabilizing the molecules can be found.

Several calculations have been carried out on the vibrational relaxation of molecules such as H_2 [8,9] and CO [10,11] at ultralow energies. Spin-changing collisions of O_2 have also been investigated [12,13]. However, collisions of alkali dimers present new theoretical challenges that are not present for collisions of stabler molecules. In particular, the potential energy surfaces are such that barrierless atom-exchange reactions can occur; even if the products are indistinguishable from the reactants, the reactive channels must be taken into account in a full treatment of the collision dynamics. Barrierless reactions are significantly different from reactions such as F + H_2 [14], which have substantial barriers and have not yet been investigated at ultralow energies. This Letter presents an initial investigation of alkali + alkali dimer collisions, for the case of Na + Na_2 collisions occurring on the lowest quartet surface for Na_3. This corresponds physically to collisions of atoms in their "stretched" spin states, with $F = F_{\max} = I + S$ and $|M_F| = F$.

In this work we use the potential energy surfaces of Higgins *et al.* [15] for the $1^4A_2'$ state of Na_3. Their full (nonadditive) potential was obtained from a grid of *ab initio* calculations with a large basis set, interpolated using the reproducing-kernel Hilbert space scheme of Ho and Rabitz [16]. The potential has a global minimum at -1222.1 K, with the atoms in an equilateral triangle configuration 4.41 Å apart. The symmetric linear geometry is a saddle point at -554.4 K (667.7 K above the minimum), with $r = 5.10$ Å. Comparison with the corresponding triplet Na_2 pair potential [17], which has $r_e = 5.192$ Å and $D_e = 255.7$ K, shows that large nonadditive effects are present. In the present work, we test the sensitivity of our results to the potential surface by performing calculations using both the full nonadditive potential and a pairwise additive potential obtained by neglecting the nonadditive part.

We initially investigated inelastic scattering calculations of vibrational relaxation from the $v = 1$ state of triplet Na_2, using the MOLSCAT program [18]. Such calculations are analogous to the H + H_2 calculations of Balakrishnan *et al.* [8] and are carried out in Jacobi coordinates (R, r, θ) for a single arrangement of the atoms. MOLSCAT expands the scattering wave function in basis functions that are eigenfunctions of the Hamiltonian for free Na_2. For Na + Na_2, however, it proved impossible to converge the basis set of Na_2 vibrational functions in three-dimensional inelastic scattering (close-coupling or coupled states) calculations. This may readily be understood in terms of the potential energy surface. Consider Na approaching Na_2 for a T-shaped geometry, $\theta = 90°$, allowing the Na_2 bond length r to relax to minimize the energy at each intermolecular distance R. The system passes through the minimum-energy equilateral geometry, and then the two atoms of the Na_2 move apart to allow the Na atom to insert between them. However, even at $R = 0$ (the linear geometry), the energy is below that for separated $Na + Na_2$. At this configuration, the optimum value of r is 10.4 Å, and the basis set of Na_2 vibrational functions centered around $r_e = 5.1$ Å is completely inadequate for representing such dramatically expanded geometries.

It is thus essential to carry out three-dimensional reactive scattering calculations, including all three atomic arrangements. As a first step towards a rigorous treatment, we have performed such calculations for total nuclear orbital angular momentum $J = 0$. The configuration space is divided into an inner and an outer region, depending on the atom-diatom distance. In the inner region, we use a formalism based on body-frame democratic hyperspherical coordinates [19]. This has previously proved successful in describing atom-diatom insertion reactions such as $N(^2D) + H_2 \rightarrow NH + H$ [20] and $O(^1D) + H_2 \rightarrow OH + H$ [21,22]. A related approach has also been used in studies of three-body recombination of ultracold atoms [23]. The scattering wave function is expanded on a set of hyperspherical adiabatic states. This yields a set of close-coupling equations, which in our method are solved using the Johnson-Manolopoulos log-derivative propagator [24]. In the outer region, we use the Arthurs-Dalgarno formalism [25], which is based on Jacobi coordinates. Matching of the wave functions in the inner and outer regions is performed on a boundary which is an hypersphere of radius 25 Å. This yields the reactance K matrix and the scattering S matrix.

The inner region starts at a hyperradius of 4 Å and is split into 297 sectors. The adiabatic states in each sector are obtained by a variational expansion on a basis of hyperspherical harmonics with A_1 symmetry. They are fully symmetric with respect to particle permutations to account for the indistinguishability of atoms. At large hyperradius, the adiabatic states concentrate into the arrangement channels and describe Na_2 molecules in even j states. At small hyperradius, they span a large fraction of configuration space and allow for atom exchange. The hyperspherical harmonic basis is truncated at Λ_{max}, the maximum value of the grand angular momentum. Λ_{max} varies from 198 (867 harmonics) at small hyperradius to 398 (3400 harmonics) at large hyperradius. A fixed number of 135 adiabatic states is used in the close-coupling expansion in each sector. At the boundary between the inner and outer regions, the adiabatic states are projected onto a set of Na_2 rovibrational states, with $j_{max} = 48, 44, 40, 36, 30, 26, 20, 10$ for vibrational levels $v = 0, 1, \ldots, 7$. The boundary between the inner and outer regions was placed at a distance such that couplings due to the atom-diatom residual interaction can be neglected outside the boundary. In the outer region, regular and irregular solutions of a radial Schrödinger equation which includes the isotropic (R^{-6}) part of the interaction were integrated inwards from very large distances (5000 Å).

Figure 1 shows the computed cross sections as a function of collision energy for the additive and nonadditive potentials. All collisions that are energetically elastic, with or without atom exchange, are included in the elastic cross section. All other processes (which produce Na_2 ($v' = 0, j'$)) contribute to the quenching cross section.

It may be seen that the Wigner threshold laws [8,26,27] hold below 10^{-5} K for both potentials. The elastic cross sections are independent of energy in the Wigner region. The cross sections are larger for the nonadditive than for the additive potential, by a factor of about 10 for both elastic and quenching cross sections. The $E^{-1/2}$ dependence of the quenching cross sections corresponds to a

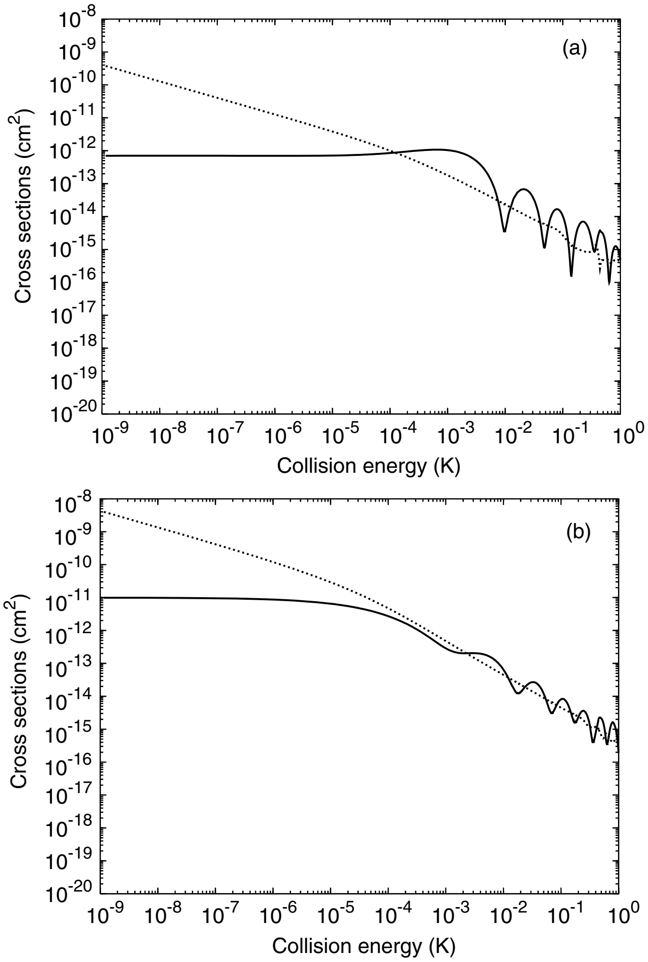

FIG. 1. Cross sections from quantum reactive scattering calculations for $Na + Na_2$ ($v = 1, j = 0$) (s-wave scattering). Elastic and quenching results are shown as solid and dotted lines. (a) Additive potential. (b) Nonadditive potential.

rate coefficient that is independent of energy below 10^{-5} K. The value is $k^{\text{inel}} = 4.8 \times 10^{-11}$ cm^3 s^{-1} for the additive potential and 5.2×10^{-10} cm^3 s^{-1} for the nonadditive potential. The corresponding complex scattering lengths [29], obtained from the diagonal element of the T matrix at a kinetic energy of 10^{-9} K, are $a = (2.26 - 0.80i)$ and $(2.38 - 8.54i)$ nm, respectively.

Outside the Wigner region, the cross sections have a more complicated energy dependence. The quenching probability increases with increasing energy and approaches unity at the limit of the Wigner region. The quenching cross sections thus vary approximately as E^{-1} above 10^{-4} K, because of the k^{-2} factor in the expression for the cross section.

The values of the quenching cross sections are quite large and suggest that vibrationally excited alkali dimers produced by photoassociation will usually be lost from a magnetic trap in a fraction of a second. However, our current calculations neglect the effects of nuclear spin and magnetic fields, which may be used to tune collisional effects. In addition, the large difference between the values for the additive and nonadditive potentials serves to emphasise the importance of using high-quality potential energy surfaces in dynamical calculations.

The ratio of quenching to elastic cross sections is larger than 1 at energies below 10^{-4} K for the additive potential and below 10^{-3} K for the nonadditive potential. It increases up to 500 in the nK range for both potentials. The ratio is not favorable for production of a Bose-Einstein condensate by evaporative cooling, though this may be circumvented by methods that produce a molecular condensate directly [6].

Na_2 rotational levels up to $j = 20$ are energetically accessible at the energy of the $v = 1$ state (23.5 cm^{-1}), and all accessible levels are populated in the products. The product rotational distributions from calculations on the additive and nonadditive potentials at 10^{-4} K are shown in Fig. 2. The distributions are essentially unchanged at lower collision energies. Only even j products are formed because of the boson symmetry. For the nonadditive potential, there are three clear maxima in the distribution, at $j = 4$, 12, and 18. The additive potential also shows an oscillatory structure, with maxima at $j =$ 0, 8, 14, and 20. The oscillations almost certainly arise from a rotational rainbow effect [29]. The structure is similar to that observed in vibrational predissociation of van der Waals complexes [30]. In a classical impulsive model, the energy released from Na_2 vibration is partly retained in relative translation and partly converted into Na_2 rotation. The angular momentum imparted to the Na_2 molecule is zero if the energy is released at a linear or T-shaped geometry, but large around $\theta = 45°$. In this model, the oscillations arise from interference between classical trajectories on either side of the maximum.

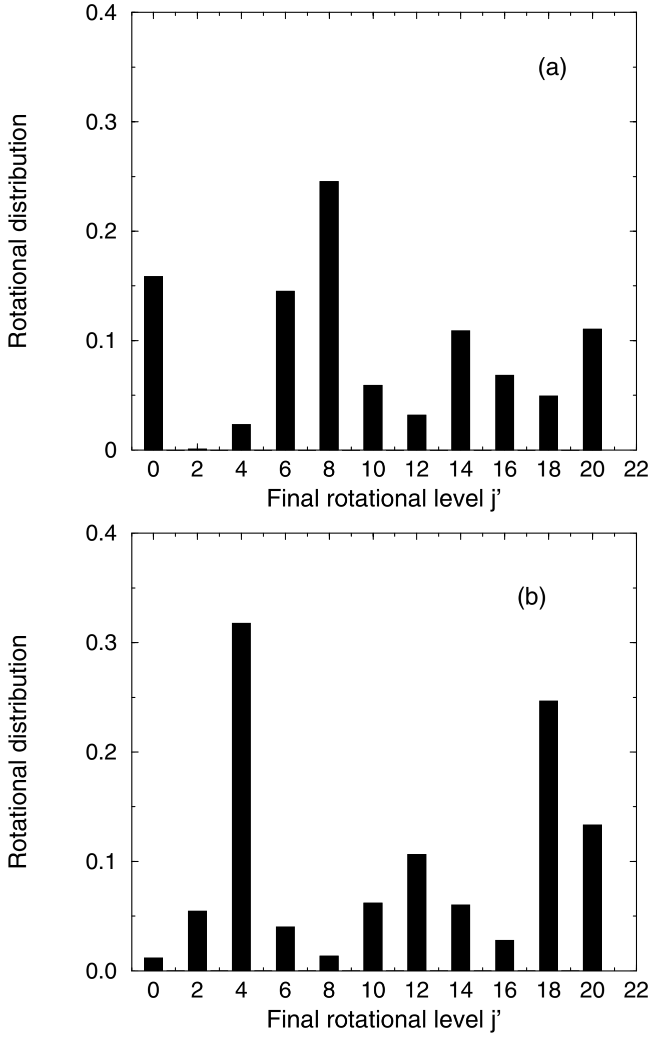

FIG. 2. Normalized rotational distributions for Na_2 products in $v' = 0$ following the quenching reaction $Na + Na_2$ $(v = 1, j = 0) \rightarrow Na + Na_2$ $(v' = 0, j')$ at a collision energy of 10^{-4} K. (a) Additive potential. (b) Nonadditive potential.

It is not yet computationally feasible to carry out reactive scattering calculations for $Na + Na_2$ for total angular momentum $J > 0$. However, we have carried out collinear inelastic scattering calculations to estimate the contributions of higher partial waves. The elastic cross sections for partial waves $l = 1$ and 2 are proportional to E^2 and E^3, respectively, for energies below 10^{-4} K, while the inelastic cross sections are proportional to $E^{1/2}$ and $E^{3/2}$, respectively, in the same energy range. The total cross sections are dominated by s-wave scattering up to about 10^{-3} K.

In future work, we intend to investigate the dependence of quenching rates on the initial vibrational quantum number and to investigate the effects of magnetic fields and nuclear spin coupling.

The three-dimensional quantum dynamical calculations were performed on a NEC-SX5 vector supercomputer, through a grant from the "Institut du Développement des Ressources en Informatique Scientifique" (IDRIS) in Orsay (France). P. S. is grateful to the EPSRC for support from research Grant No. GR/R17522/01. J. M. H. is grateful to JILA, University of Colorado and National Institute of Standards and Technology, for its hospitality in 2001–2002.

[1] W. C. Stwalley and H. Wang, J. Mol. Spectrosc. **195**, 194 (1999).

[2] R. Wynar, R. S. Freeland, D. J. Han, C. Ryu, and D. J. Heinzen, Science **287**, 1016 (2000).

[3] J. M. Gerton, D. Strekalov, I. Prodan, and R. G. Hulet, Nature (London) **408**, 692 (2000).

[4] C. McKenzie *et al.*, Phys. Rev. Lett. **88**, 120403 (2002).

[5] F. H. Mies, E. Tiesinga, and P. S. Julienne, Phys. Rev. A **61**, 022721 (2000).

[6] E. A. Donley, N. R. Claussen, S. T. Thompson, and C. E. Wieman, Nature (London) **417**, 529 (2002).

[7] D. J. Heinzen *et al.* (unpublished).

[8] N. Balakrishnan, R. C. Forrey, and A. Dalgarno, Chem. Phys. Lett. **280**, 1 (1997).

[9] N. Balakrishnan, R. C. Forrey, and A. Dalgarno, Phys. Rev. Lett. **80**, 3224 (1998).

[10] N. Balakrishnan, A. Dalgarno, and R. C. Forrey, J. Chem. Phys. **113**, 621 (2000).

[11] C. Zhu, N. Balakrishnan, and A. Dalgarno, J. Chem. Phys. **115**, 1335 (2001).

[12] J. L. Bohn, Phys. Rev. A **62**, 032701 (2000).

[13] A. V. Avdeenkov and J. L. Bohn, Phys. Rev. A **64**, 052703 (2001).

[14] N. Balakrishnan and A. Dalgarno, Chem. Phys. Lett. **341**, 652 (2001).

[15] J. Higgins, T. Hollebeek, J. Reho, T.-S. Ho, K. K. Lehmann, H. Rabitz, and G. Scoles, J. Chem. Phys. **112**, 5751 (2000).

[16] T.-S. Ho and H. Rabitz, J. Chem. Phys. **104**, 2584 (1996).

[17] M. Gutowski, J. Chem. Phys. **110**, 4695 (1999).

[18] J. M. Hutson and S. Green, MOLSCAT computer program, version 14, 1994, distributed by Collaborative Computational Project No. 6 of the U.K. Engineering and Physical Sciences Research Council. Some modifications were made to improve the efficiency for ultracold collisions.

[19] J.-M. Launay and M. Le Dourneuf, Chem. Phys. Lett. **163**, 178 (1989).

[20] P. Honvault and J.-M. Launay, J. Chem. Phys. **111**, 6665 (1999).

[21] P. Honvault and J.-M. Launay, J. Chem. Phys. **114**, 1057 (2001).

[22] F. J. Aoiz, L. Bañares, J. F. Castillo, M. Brouard, W. Denzer, C. Vallance, P. Honvault, J.-M. Launay, A. J. Dobbyn, and P. J. Knowles, Phys. Rev. Lett. **86**, 1729 (2001).

[23] B. D. Esry, C. H. Greene, and J. P. Burke, Jr., Phys. Rev. Lett. **83**, 1751 (1999).

[24] D. E. Manolopoulos, J. Chem. Phys. **85**, 6425 (1986).

[25] A. M. Arthurs and A. Dalgarno, Proc. R. Soc. London A **256**, 540 (1960).

[26] E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

[27] H. R. Sadeghpour, J. L. Bohn, M. J. Cavagnero, B. D. Esry, I. I. Fabrikant, J. H. Macek, and A. R. P. Rau, J. Phys. B **33**, R93 (2000).

[28] N. Balakrishnan, V. Kharchenko, R. C. Forrey, and A. Dalgarno, Chem. Phys. Lett. **280**, 5 (1997).

[29] R. Schinke and P. McGuire, J. Chem. Phys. **71**, 4201 (1979).

[30] J. M. Hutson, C. J. Ashton, and R. J. Le Roy, J. Phys. Chem. **87**, 2713 (1983).